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Organometallic Chemistry of Ethynyl Boronic Acid MIDA Ester, HC≡CB(O$_2$CCH$_2$)$_2$NMe.†

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The reactions of HC≡CBMIDA (BMIDA = B(O$_2$CCH$_2$)$_2$NMe) with a range of ruthenium complexes afford the first isolated examples of σ-alkynyl, σ-alkenyl and vinylidene complexes bearing 4-coordinate boron substituents. Specifically, the reactions of HC≡CBMIDA with [RuH(S$_2$CNR$_2$)(CO)(PPh$_3$)$_2$] and [Ru(CO)$_2$(PPh$_3$)$_3$] afford the alkynyl complexes [Ru(C≡CBMIDA)(S$_2$CNR$_2$)(CO)(PPh$_3$)$_2$] and [RuH(C≡CBMIDA)(CO)$_2$(PPh$_3$)$_2$], the latter being converted to [Ru(C≡CBMIDA)Cl(CO)$_2$(PPh$_3$)$_2$] on treatment with chloroform. With [RuCl(dppe)$_2$]PF$_6$ the vinylidene salt [RuCl(=C=CHBMIDA)(dppe)$_2$]PF$_6$ is obtained, which reacts with Et$_3$N to afford the neutral alkynyl derivative [Ru(C≡CBMIDA)Cl(dppe)$_2$]. Hydrometallation of HC≡CBMIDA by [RuHCl(CO)(PPh$_3$)$_3$] affords the coordinatively unsaturated σ-alkenyl complex [RuCl(CH=CHBMIDA)(CO)(PPh$_3$)$_2$] which in turn reacts with CO, CNC$_6$H$_2$Me$_3$-2,4,6, [Et$_2$NH$_2$][S$_2$CNEt$_2$] or K[HB(pz)$_3$] (pz = pyrazol-1-yl) to afford the coordinatively saturated complexes [Ru (CH=CHBMIDA)Cl(CO)$_2$(PPh$_3$)$_2$], [Ru(CH=CHBMIDA)Cl(CO)(CNC$_6$H$_2$Me$_3$)(PPh$_3$)$_2$], [Ru(CH=CHBMIDA)(S$_2$CNEt$_2$)(CO)-(PPh$_3$)$_2$] and [Ru(CH=CHBMIDA)(CO)(PPh$_3$){HB(pz)$_3$}]. In all cases, the transannular N→B dative bond is retained in the BMIDA substituent.

Introduction

Amongst the broadening range of boron-based transmetallation agents for metal mediated cross-coupling reactions,[1] boronic acid N-Methyliminodiacetic esters, R–B(O$_2$CCH$_2$)$_2$NMe (hereafter R–BMIDA, Figure 1), are attracting increasing interest.[2] The primary feature of note is that the tetrahedral boron is held within a conformationally rigid cage structure by a transannular dative (polar-covalent) N→B bond which attenuates the reactivity of the C–B bond in Suzuki-Miyaura processes, until the boronic acid is revealed, when required, by hydrolysis under mild conditions.

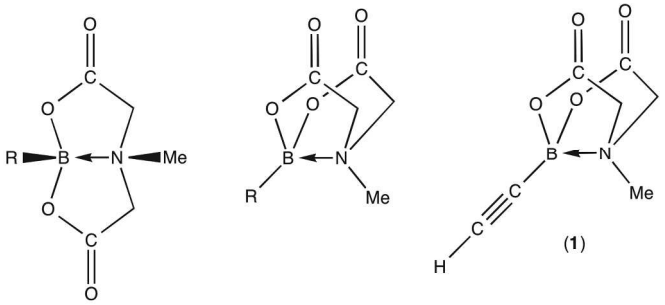
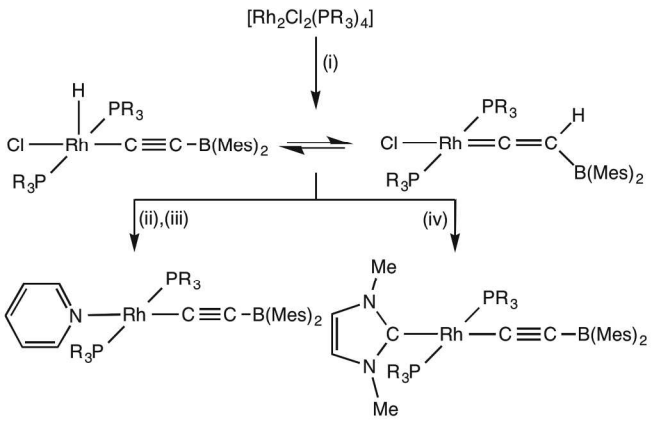


Fig. 1 R-BMIDA esters

Alkynes provide key entry points to a diversity of σ-C$_1$ ligands for organotransition metal chemistry including σ-alkynyls, σ-alkenyls, carbynes, vinylidenes and allenylidenes, however the organometallic chemistry of boron-functionalised alkynes is comparatively unexplored. Siebert has described the cyclotrimerisation of catechol substituted boryl acetylenes (e.g., C$_2$B(O$_2$C$_6$H$_4$)$_2$ = CatB-C≡C-BCat) by [Co$_2$(CO)$_8$], [Ni(cod)$_2$] and [Co(CO)$_2$(η-C$_5$H$_5$)], the former via a dicobaltatetrahedrane [Co$_2${μ-C$_2$(BCat)$_2$}(CO)$_6$] which could be isolated and reintroduced into the catalytic cycle.[3] More recently, Braunschweig reported the reaction of [Rh$_2$Cl$_2$(P^{i}Pr$_3$)$_4$] with HC≡CBMes$_2$ (Mes = C$_6$H$_2$Me$_3$-2,4,6)[4] to afford a rare[5] example of a boron-functionalised vinylidene complex [RhCl(=C=CHBMes$_2$)(P^{i}Pr$_2$)$_2$] and the only one to arise from rearrangement of a pre-formed alkynylborane. Dehydrochlorination of this complex by either pyridine/LiN^{i}Pr$_2$ or dimethylimidazol-2-ylidene (IMe) provided the first examples of borylalkynyl ligands in the complexes [Rh(C≡CBMes$_2$)(L)(P^{i}Pr$_3$)$_2$] (L = py, IMe, Scheme 1). An intriguing aspect of the organometallic chemistry of alkynylboranes is the possibility of the boron centre interacting directly with a metal centre, as illustrated by Stephan with the isolation of the complex [Ni{η^3-*B,C,C'*-^{t}Bu$_2$PC≡CB(C$_6$F$_5$)$_2$}(η^4-cod)], which may be described as involving a dative Ni→B interaction.[6a] Alternatively, the electrophilic boron may interact with a co-ligand, e.g., the hydride in [Ru(μ-H){PhC≡CB(C$_6$F$_5$)$_2$}(PPh$_3$)(η-C$_5$H$_5$)] (Figure 2) which forms a 3-centre, 2-electron B–H–Ru interaction.[6b]



Scheme 1 Braunschweig's synthesis of β-boryl vinylidene and alkynyl complexes (Mes = $C_6H_2Me_3$-2,4,6).[4] (i) H≡CBMes; (ii) py; (iii) LiN^iPr_2; (iv) $C(NMeCH)_2$.

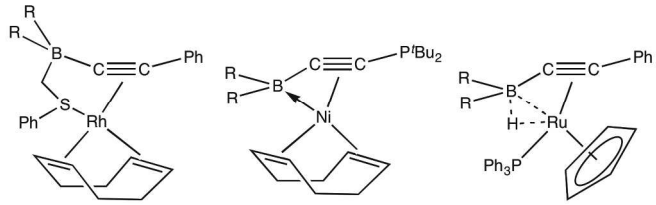


Fig. 2 Non-innocent boryl involvement in alkynylborane coordination (R = C_6F_5).[6]

Each of these investigations involve alkynylboranes in which the boron is 3-coordinate, raising the question as to whether alkynes bearing 4-coordinate boron centres, e.g., ethynylBMIDA (**1**) might display interesting coordination chemistry. We report herein, an exploration of the reactivity of **1** towards a range of low-valent ruthenium substrates, which afford the first examples of alkynyl, alkenyl and vinylidene ligands bearing 4-coordinate boron (BMIDA) substituents. Previously, both the [RuCl(cod)(η-C_5Me_5)] mediated cycotrimerisation of **1** with diynes[2m] and the [Rh_2Cl_4(η-$C_5Me_5)_2$] mediated annulation of pivaloylbenzamides with **1**[2n] have been reported though no intermediates were pursued.

Results and discussion

Computational analysis of **1** (M06/6-31G*) returns a near degenerate HOMO/HOMO-1 set that is primarily associated with the alkynyl triple bond (Figure 3), whilst the LUMO+2/LUMO+3 set comprise the antibonding (π*) orbitals of the same bond and whilst these are comparatively high in energy and unlikely to be effective π-acceptors in a Dewar-Chatt-Duncanson sense, it is noteworthy that they comprise considerable Bπ-Cπ overlap. The LUMO and LUMO+1 are primarily associated with BMIDA cage.

σ-Alkynyl and Vinylidene Complexes.

The reactions of the complex [$Ru(CO)_2(PPh_3)_3$] (**2**)[7] with internal alkynes proceed via phosphine substitution to afford simple π-adducts, metallacyclopentadienes or cyclopentadienones via alkyne coupling processes.[8] With terminal alkynes, HC≡CR, C–H activation preferentially occurs, albeit reversibly, to provide hydrido-alkynyl complexes [$RuH(C{\equiv}CR)(CO)_2(PPh_3)_2$].[9] The reaction of **2** or synthetically equivalent [$Ru(\eta^2\text{-}C_2H_4)(CO)_2(PPh_3)_2$] (**3**) with **1** in dichloromethane proceeds rapidly to provide the octahedral alkynyl complex [$RuH(C{\equiv}CBMIDA)(CO)_2(PPh_3)_2$] (**4**, Scheme 2).

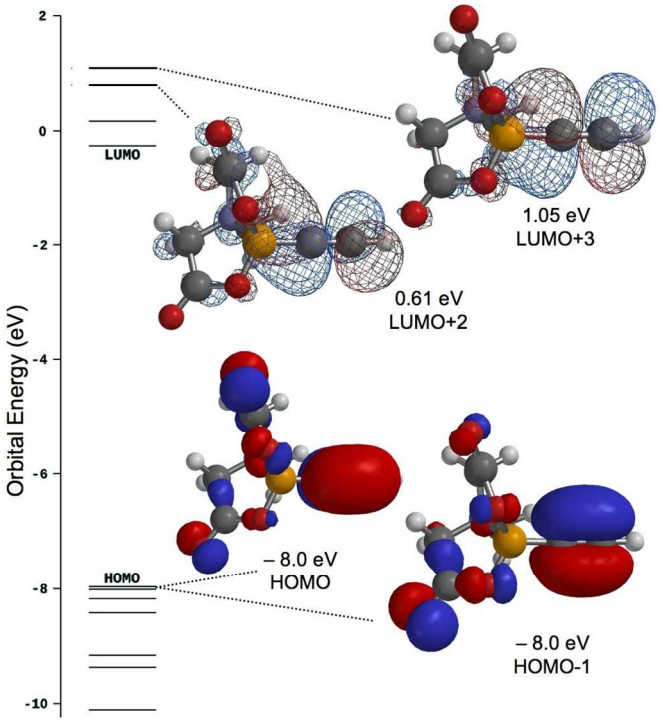
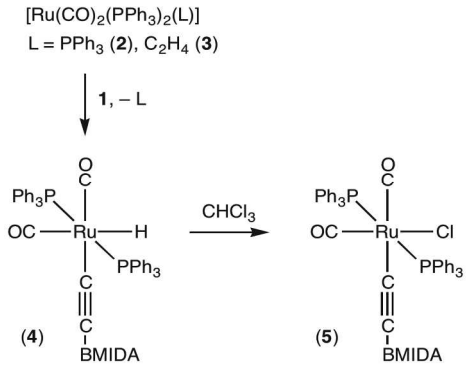


Fig. 3 Frontier orbitals of interest for HC≡CBMIDA (**1**)

The spectroscopic data characterizing **4** include the appearance of two ν_{CO} absorptions in the infrared spectrum at 2032 and 1988 cm^{-1} in CH_2Cl_2. Weaker absorptions at 2081 and 1951 cm^{-1} are tentatively attributed to ν_{CC} and ν_{RuH}, respectively whilst noting that these will to some extent be coupled with the ν_{CO} modes.



Scheme 2 Reactions of HC≡CBMIDA (**1**) with zerovalent ruthenium complexes.

The presence of the hydride ligand is more definitively evident in the ^1H NMR spectrum, which includes a high-field

triplet resonance (δ_H = –5.87, $^2J_{PH}$ = 20.2 Hz). The BMIDA group gives rise to a single resonance due to the NCH_3 group (1.80 ppm) in addition to two doublets at 2.77 and 3.21 ppm ($^2J_{HH}$ = 16.0 Hz) corresponding to the *endo* and *exo* NCH_2 protons indicating that the BMIDA cage rotates freely about the C–B bond. These general spectroscopic features of the BMIDA group were essentially invariant for the compounds to be described and call for no further comment. The characterization of **4** included a crystal structure determination, the results of which are summarised in Figure 4. The *pseudo*-octahedral geometry about ruthenium involves a modest distortion of the two bulky phosphines towards the hydride ligand (P1–Ru1–P2 = 167.60(4)°) the position of which was located but not refined. The alkynyl ligand of interest is close to linear with a small bending of the BMIDA substituent (C1–C2–B2 = 171.5(8)°) so as to accommodate and minimize inter-ligand non-bonding interactions with the two phosphines. The Ru1–C1 and C1–C2 bond lengths are not significantly different from those observed for other complexes of the form $[RuH(C{\equiv}CR)(CO)_2(PPh_3)_2]$ (R = C≡CH,[9a] $^+PPh_3$,[9b] $SiMe_3$[9c]).

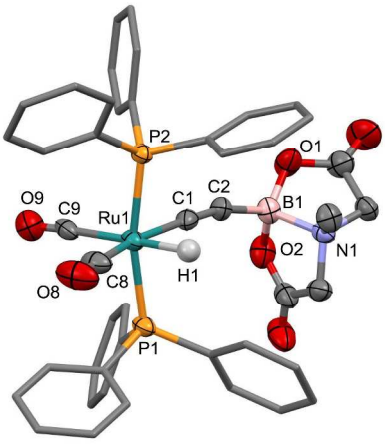


Fig. 4 Molecular structure of **4** with 50% probability displacement ellipsoids. For clarity, most hydrogen atoms have been omitted and phenyl groups simplified. Selected bond distances [Å] and angles [°]: Ru1–C1 2.060(7), Ru1–H1 1.560, Ru1–C8 1.899(8), Ru1–C9 1.955(8), C1–C2 1.21(1), B1–C2 1.54(1), B1–N1 1.666(9), Ru1–C1–C2 178.1(6), C1–C2–B2 171.5(8).

The geometrical features of the BMIDA cage in **4** do not differ markedly from those of **1**, which was structurally characterised for comparative purposes (Figure 5). The B–C bond lengths in **1** (1.554(7) Å) and **4** (1.54(1)Å) are not significantly different.

Although **4** is stable in benzene or dichloromethane solution in the absence of air, when dissolved in chloroform immediate quantitative conversion to the corresponding chloro derivative $[RuCl(C{\equiv}CBMIDA)(CO)_2(PPh_3)_2]$ (**5**) occurs, accompanied by an increase in the frequencies of the ν_{CO} (CH_2Cl_2: 1995, 2058) and ν_{CC} (2080 cm^{-1}) infrared absorptions.

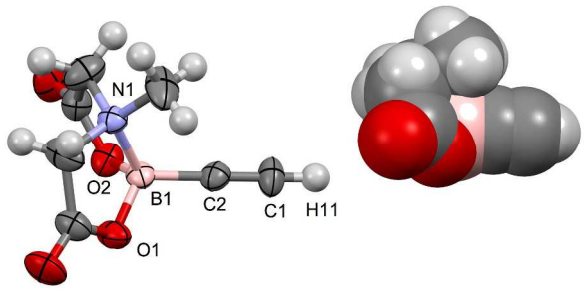
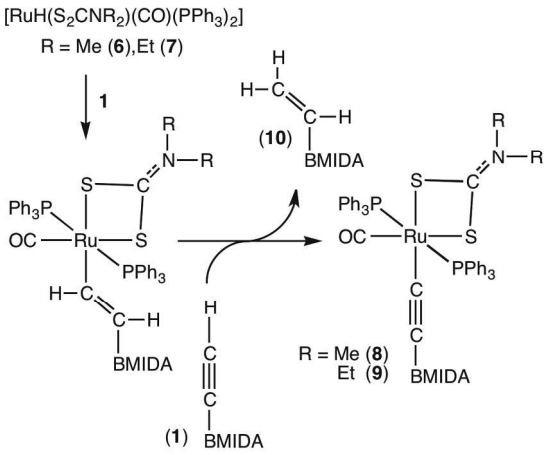


Fig. 5 Molecular structure of **1** with 50% probability displacement ellipsoids. Selected bond distances [Å] and angles [°]: B1–N1 1.635(6), B1–O1 1.458(6), B1–O2 1.469(6), B1–C2 1.554(7), C1–C2 1.176(6), C2–C1–H11 179.0, B1–C2–C1 175.8(5).

An alternative approach to installing the alkynyl ligand involves the reaction of the terminal alkynes with divalent ruthenium hydride complexes $[RuH(S_2CNR_2)(CO)(PPh_3)_2]$ (R = Me **6**, Et **7**).[10] Thus heating **6** or **7** with an excess of **1** results in the formation of the alkynyl complexes $[Ru(C{\equiv}CBMIDA)(S_2CNR_2)(CO)(PPh_3)_2]$ (R = Me **8**, Et **9,** Scheme 3).



Scheme 3. Hydrometallation/Ru–C σ-metathesis route to alkynyl BMIDA complexes.

The more π-basic nature of the ruthenium centres in **8** and **9** is reflected in the comparatively low frequencies for both the ν_{CO} (**8**: 1943; **9**: 1945 cm^{-1}) and ν_{CC} (**8**: 2057; **9**: 2062 cm^{-1}) infrared absorptions, whilst the restricted rotation of the dithiocarbamate amino groups about the N-C bond is reflected in the observation of chemically inequivalent substituents on the ^1H NMR timescale. Both complexes were structurally characterised and the results obtained for **8** are depicted in Figure 6.

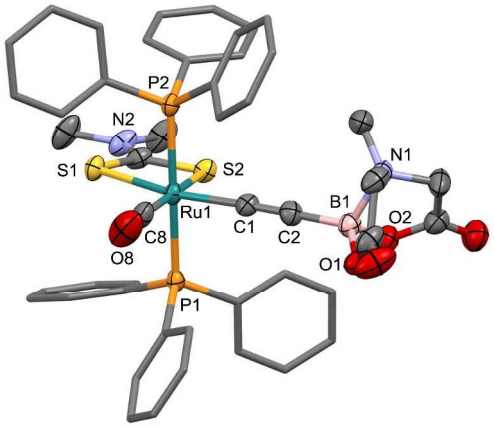


Fig. 6 Molecular structure of **8** with 60% probability displacement ellipsoids. For clarity, hydrogen atoms have been omitted and phenyl groups simplified. Selected bond distances [Å] and angles [°]: Ru1–C1 2.030(3), Ru1–C8 1.842(3), Ru1–S1 2.4549(6), Ru1–S2 2.4734(7), C1–C2 1.202(4), B1–C2 1.539(4), B1–N1 1.674(4), C8–O8 1.126(4), Ru1–C1–C2 178.0(2), S1–Ru1–S2 71.32(2), C1–C2–B1 172.9(3).

The Ru1–C1 bond length of 2.030(3)Å is marginally shorter than observed for **4** though the C1–C2 and C2–B1 bond lengths are not significantly different to the corresponding bonds in the dicarbonyl derivative. The alkynyl ligand displays a weaker *trans* influence than does the CO ligand, as reflected in Ru1–S1 (2.4549(6)Å) being significantly (30 e.s.d.) shorter than Ru1–S2 (2.4734(7)Å). As with **4**, there is a modest deviation from linearity at C2.

The mechanism for the formation of **8** and **9** is presumed to involve hydroruthenation of the alkyne to provide the σ-alkenyl complexes [Ru(CH=CHBMIDA)(S_2CNR_2)(CO)(PPh_3)$_2$] which then undergo Ru–C σ- bond metathesis to form the more stable alkynyl complexes with release of H_2C=CHBMIDA (**10**).[2j] It is a caveat of the hydrometallation step that phosphine dissociation is necessary to provide a vacant coordination site for alkyne coordination, requiring heating (CH_2Cl_2 reflux) and prolonged reaction times (36 h).

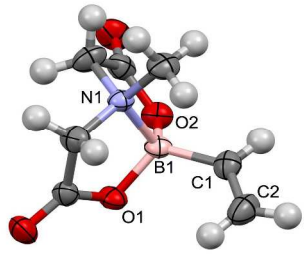
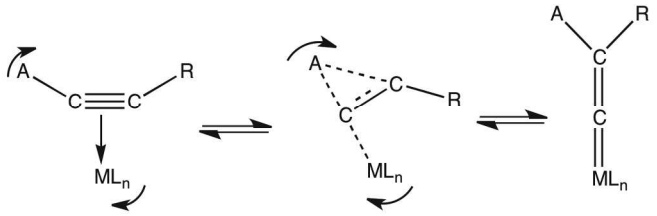


Fig. 7 Molecular structure of **10** with 50% probability displacement ellipsoids. Selected bond distances [Å] and angles [°]: B1–N1 1.648(2), B1–O1 1.480(2), B1–O2 1.473(2), B1–C2 1.577(3), C1–C2 1.299(3), B1–C2–C1 127.3(2).

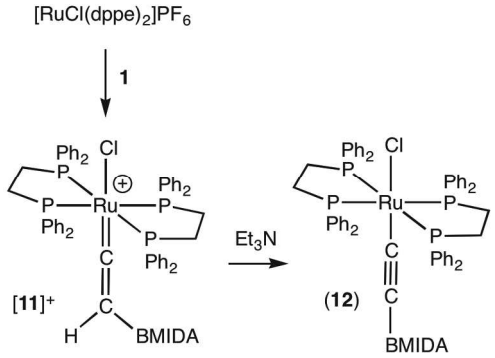
Under these conditions, the subsequent cleavage of the σ-alkenyl ligand by extraneous **1** precludes the proposed intermediate σ-alkenyl complexes being isolated. Evidence is provided for the mechanistic proposal by the isolation and structural characterization of **10** (Figure 7) from the reaction mixtures. Further support comes from the synthesis of one of the intermediates via an alternative strategy and its subsequent conversion to **9** (*vide infra*).

The reversible rearrangement of alkynes to vinylidene ligands (Scheme 4) is commonly observed for d^6-ruthenium centres and may be traced in part to the elimination of the π-donor capacity of alkynes potentially destabilizing their binding to metals with high d-occupancies. The migrating group (A, Scheme 4) is most commonly a proton,[11] however carbon and a range of hetero atoms (A = C, Si, Sn, S, Se, I)[12] have been observed to undergo what is generally considered to be a concerted 1,2-migration.[13] Although it remains to be demonstrated, it would seem likely that this avenue would be favorable for boryl substituents given the availability of a Lewis acidic orbital on the 3-coordinate boron.



Scheme 4 Alkyne-vinylidene rearrangement (A = H, SiR_3, SnR_3, SR, SeR, I).[11,13]

The salt [RuCl(dppe)$_2$]PF_6 has been employed extensively in the study of vinylidene chemistry[14] and was found here to react cleanly with **1** to afford the boryl vinylidene salt [RuCl(=C=CHBMIDA)(dppe)$_2$]PF_6 ([**11**]PF_6, Scheme 5).



Scheme 5 BMIDA Vinyidene and alkynyl complexes

As with other examples,[14] the geometry about ruthenium (Figure 8) involves the *trans* disposition of chloro and vinylidene ligands, as indicated by the appearance of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum (δ_P = 45.5) other than the characteristic PF_6 resonance. Amongst the characterisational data for [**11**]$^+$, the most informative is the low-field pentet resonance at δ_C = 334.7 ($^2J_{PC}$ = 10.2 Hz) corresponding to the ruthenium bound carbon (Cα) of the vinylidene ligand. This value may be compared with that for Braunschweig's vinylidene [Rh(=Cα=CβHBMes$_2$)Cl(P^{i}Pr$_3$)$_2$] at δ_C = 300.7 ($^2J_{PC}$ = 12.1 Hz).[4] The crystal structure of the solvate [**11**]PF_6.CH_2Cl_2 (Figure 8) confirms the formulation and *trans*-

octahedral geometry at ruthenium. A comparison of the Ru1–C1 (1.844(5)Å) and C1–C2 (1.310(7)Å) bond lengths with those for $[Ru(=C=CHC_6H_4NPh_2)(dppe)_2]PF_6$[14h] (1.844(2), 1.313(3)Å, respectively) indicates that the BMIDA group does not induce any unusual geometric perturbations relative to a more conventional hydrocarbyl vinylidene substituent. There is however a conspicuous distortion in the C1-C2-B1 angle (138.5(6)°) from the ideal 120° expected for an sp^2-hybridised carbon centre which is most likely due to the considerable steric bulk of the BMIDA group.

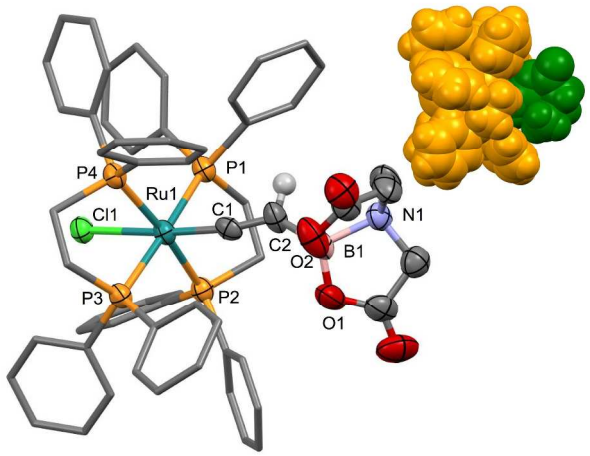
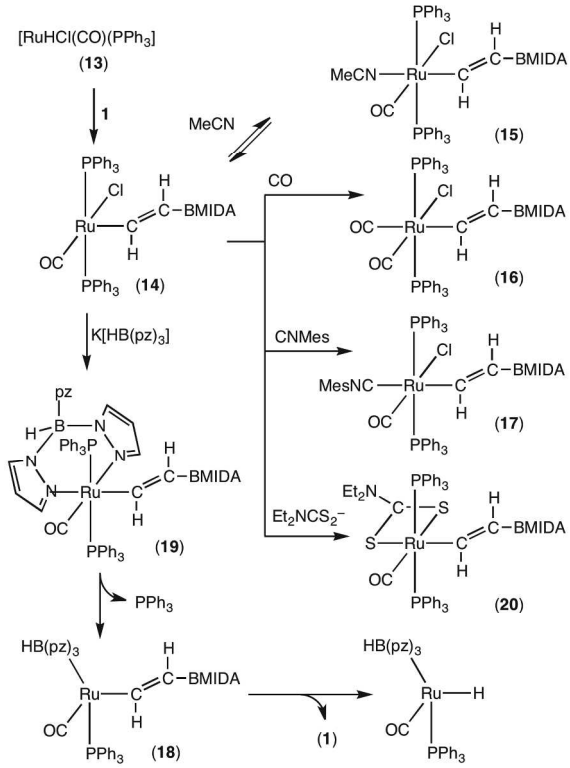


Fig. 8 Molecular structure of $[\mathbf{11}]^+$ in a crystal of $[\mathbf{10}]PF_6{\cdot}CH_2Cl_2$ with 50% probability displacement ellipsoids. For clarity, most hydrogen atoms, the solvent and PF_6^- counteranion have been omitted and phenyl groups simplified. Selected bond distances [Å] and angles [°]: Cl1–Ru1 2.4664(13), Ru1–C1 1.844(5), C1–C2 1.310(7), P1–Ru1 2.4101(15), P2–Ru1 2.3906(16), P3–Ru1 2.4315(15), P4–Ru1 2.4380(16), Ru1–C1–C2 168.9(5), B1–C2–C1 138.5(6). Inset: Space-filling representation showing CCHBMIDA (green) surrounded by the sterically demanding $RuCl(dppe)_2$ cradle (gold).

Typical of cationic vinylidene complexes, the reaction of $[\mathbf{11}]PF_6$ with Et_3N results in deprotonation to afford the alkynyl complex $[RuCl(C{\equiv}CBMIDA)(dppe)_2]$ (**12**). The poor solubility of **12** in common solvents compromised the acquisition of some spectroscopic data and samples appeared to be contaminated with $[Et_3NH]PF_6$. Nevertheless, a characteristic and strong ν_{CC} (KBr: 2024 cm^{-1}) absorption was observed in the infrared spectrum (*cf.* 2070 cm^{-1} for $RuCl(C{\equiv}CC_6H_4NPh_2)(dppe)_2]$[14h]), whilst ^{11}B (5.4 ppm) and ^{31}P (47.8 ppm) NMR signals were in the expected regions. The most intense peak in the ESI (+ve ion, acc. mass) mass spectrum corresponded to $[M\text{-}Cl{+}NCMe]^+$ (*m/z* = 1119.2485) arising from halide displacement by the acetonitrile matix, as is commonly observed for ruthenium chloro complexes under ESI conditions. The use of 'bench-top' DBU in place of Et_3N resulted in a mixture of the previously reported compounds $[RuCl(=C=CH_2)(dppe)_2]PF_6$ (δ_P = 41.5) and $[RuCl(C{\equiv}CH)(dppe)_2]$ (δ_P = 49.3)[14e] due to hydrolysis of the vinylidene ligand. The former was previously obtained by presumed hydrolysis of the silylvinylidene $[RuCl(=C=HCSiMe_3)(dppe)_2]PF_6$, most likely facilitated by the cationic nature of the complex.

σ-Alkenyl Complexes.

The cyclotrimerisation of **1** with diynes[2m] and the annulation of pivoloylbenzamides with **1**[2n] most likely proceed via metallacyclic alkenyl intermediates bearing BMIDA substituents, however no attempt to isolate such species have been made. The hydroruthenation of **1** to afford a σ-alkenyl complex was proposed *en route* to the formation of complexes **8** and **9** (Scheme 3). Accordingly, the isolation of such species was investigated with recourse to the complex $[RuHCl(CO)(PPh_3)_3]$ (**13**).[15] By virtue of the lability of one phosphine in solution, complex **13** is able to readily hydroruthenate alkynes, diynes, phospha-alkynes and dimetallaoctatetraynes.[16-18] In the case of terminal alkynes (RC≡CH), the reactions typically proceed regioselectively at room temperature to afford the coordinatively unsaturated σ-alkenyl complexes $[Ru(trans\text{-}\beta\text{-}CH{=}CHR)(CO)(PPh_3)_2]$. For **1**, this is the predominant course of the reaction with **13** to afford $[Ru(CH{=}CHBMIDA)Cl(CO)(PPh_3)_2]$ (**14**, Scheme 6), however we are aware of the formation of small amounts of what appears to be a regioisomer (**14a**).



Scheme 6 Synthesis of BMIDA functionalised σ-alkenyl complexes

Whilst **14a** could be successfully removed from **14** by fractional crystallization and extensive washing, it was not itself isolated in pure form such that its identity remains equivocal (*vide infra*). Spectroscopic data for **14** confirm the *cis*-hydroruthenation of the alkyne as expected for a concerted insertion of the pre-coordinated alkyne into the Ru–H bond. The vinylic **AB** system is evident in the ^1H NMR spectrum as two doublets at δ_H = 5.10 and 8.44 with $^3J_{HH}$ = 12.9 Hz being in the range typical of a *trans*-substituted alkene. The ESI mass spectrum has as the most intense peaks $[M\text{-}Cl]^+$ and [M-

Cl+NCMe]$^+$, the latter arising from coordination of the acetonitrile matrix. This is reflected in acetonitrile solutions of **14** from which may be precipitated [Ru(CH=CHBMIDA)Cl(NCMe)(CO)(PPh_3)$_2$] (**15**). This *solvento* complex when redissolved in solvents other than acetonitrile (benzene, CH_2Cl_2, THF) rapidly reforms **14**.

Whilst acetonitrile coordination is readily reversible, carbon monoxide and mesityl isonitrile coordinate to **14** to provide the stable 18-electron complexes [Ru(CH=CHBMIDA)Cl(L)-(CO)(PPh_3)$_2$] (L = CO **16**, CNMes **17**), with no indication of the operation of migratory insertion processes. This is in contrast to the σ-tolyl complex [Ru(C_6H_4Me-4)Cl(CO)(PPh_3)$_2$] which upon addition of CO[19] or isonitriles[20] results in the formation of toluyl or iminotoluyl complexes and addition of ^{t}BuNC to [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] affords the cationic cinnamoyl complex [Ru{C(=O)CH=CHPh}(CN^tBu)$_3$-(PPh_3)$_2$]$^+$.[21] Whilst full characterization of **17** was possible, the very poor solubility of **16** compromised the acquisition of some solution spectroscopic data. Attempts to obtain crystallographic grade crystals of **16** via recrystallisation were similarly confounded by this poor solubility, however single crystals were obtained by slow diffusion of head-space CO, without agitation, into a solution of **14** in a narrow (NMR) tube. Whilst the crystallographic model was of low precision due to poor data, the connectivity was nevertheless established beyond doubt (Figure 9).

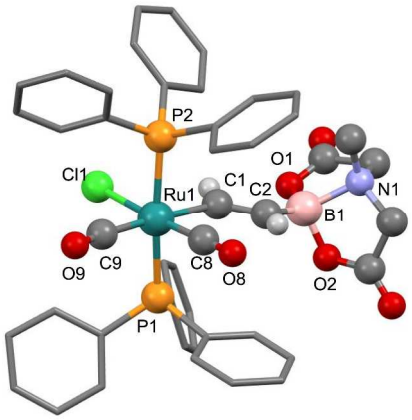


Fig. 9 Molecular structure of **16**. Whilst confirming the connectivity and gross geometry, the low precision of the structural model precludes detailed interpretation of the geometrical parameters.

The reaction of **14** with K[HB(pz)$_3$] (pz = pyrazol-1-yl) results in the formation of the complex [Ru(CH=CHBMIDA)(CO)(PPh_3){κ^3-HB(pz)$_3$}] (**18**) by analogy with related σ-aryl and σ-alkenyl complexes.[22] The chirality of the complex is reflected in the observation of three distinct pyrazolyl environments in the ^{1}H NMR spectrum of **18**. During the formation of **18**, an intermediate [Ru(CH=CHBMIDA)(CO)(PPh_3)$_2${κ^2-HB(pz)$_3$}] (**19**) could be observed (^{31}P{^{1}H} NMR), though not isolated due to its slow but spontaneous conversion to **18**. In complex **19** the HB(pz)$_3$ scorpionate is presumed to adopt a bidentate coordination mode, thereby destroying the equatorial mirror plane present in **14** and resulting in chemically inequivalent phosphorus nuclei (δ_P = 42.57, 47.03) which are strongly coupled ($^2J_{PP}$ = 304 Hz), consistent with their mutually *trans* disposition. We have previously observed similar intermediates in the formation of [RuH(CO)(PPh_3){κ^3-HB(pz)$_3$}] and [Os(C_6H_5)(CO)(PPh_3){HB(pz)$_3$}][23] from K[HB(pz)$_3$] with [RuHCl(CO)(PPh_3)$_3$] and [OsCl(C_6H_5)(CO)(PPh_3)$_2$], respectively. In contrast to other σ-alkenyl complexes of the form [Ru(CH=CHR)(CO)(PPh_3){HB(pz)$_3$}] which are indefinitely stable, solutions of **18** decompose completely over 24 hours to provide **1** and [RuH(CO)(PPh_3){HB(pz)$_3$}]. Whilst a simple β-Ru–H elimination (requiring *hemi-labile* HB(pz)$_3$ coordination) accounts for this transformation, we are unable to suggest why it should occur in the case of **18** but not for other more conventional σ-alkenyl ligands.

As noted above, σ-alkenyl intermediates were invoked in the conversion of [RuH(S_2CNR_2)(CO)(PPh_3)$_2$] to the alkynyl complexes **8** and **9** (Scheme 3). To confirm this supposition, the reaction of **14** with [Et_2NH_2][S_2CNEt_2] was investigated and found, as expected,[24] to afford the complex [Ru(CH=CHBMIDA)(S_2CNEt_2)(CO)(PPh_3)$_2$] (**20**). Spectroscopic data for **20** were unremarkable, other than to note, as for **8** and **9**, that the dithiocarbamate substituents are chemically inequivalent due to the restricted rotation about the N–C bond. The ν_{CO} absorption observed in the infrared spectrum of **20** (1912 cm^{-1}) appears to lower frequency of that for the corresponding alkynyl **9** (1945 cm^{-1}) consistent with the alkynyl being a stronger π-acceptor. Some caution is however required in that coupling of the ν_{CC} (2062 cm^{-1}) and ν_{CO} oscillators is likely, thereby clouding direct comparison. Just as in the case of **18**, the dithiocarbamato complex **20** was found to decompose in solution, albeit more slowly. This frustrated attempts to obtain crystallographic grade crystals of **20** and before ultimately succeeding, numerous crystal modifications of the decomposition product [RuCl(S_2CNEt_2)(CO)(PPh_3)$_2$] (**21**) were obtained (see Experimental Section). Presumably, facile β-Ru–H elimination to generate [RuH(S_2CNEt_2)(CO)(PPh_3)$_2$] (**7**) is followed by reaction with the chlorinated solvent (CH_2Cl_2, $CHCl_3$). Nevertheless, the structure of **20** was eventually crystallographically confirmed with crystals of the monosolvate obtained from acetone (Figure 10).

The asymmetric unit contains three crystallographically distinct molecules of **20** (Z = 12), however metrical parameters do not vary significantly between individual molecules. The structure confirms the overall geometry as well as the trans-β-regiochemistry of the alkenyl ligand. In principle there are two possible orientations of the vinyl ligand, however that adopted does allow a weak hydrogen bonding approach by the proton (H21) to one of the dithiocarbamate sulfur atoms (H21···S1 = 2.608 Å). The Ru1–C1 bond length (2.123(8)Å) is marginally longer than that found in the corresponding alkynyl complex **9** (2.044(4), 2.058(4)Å) reflecting the increased coordination at C1 and decreased Ru—C bond strength. The σ-alkenyl ligand exerts a pronounced *trans* influence (Ru1–S2 = 2.517(2)Å) *cf.*

the corresponding Ru–S bond length in the alkynyl complex **9** (2.4688(8)Å).

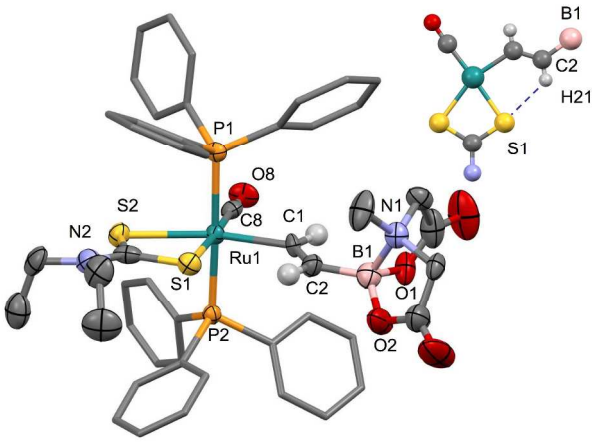
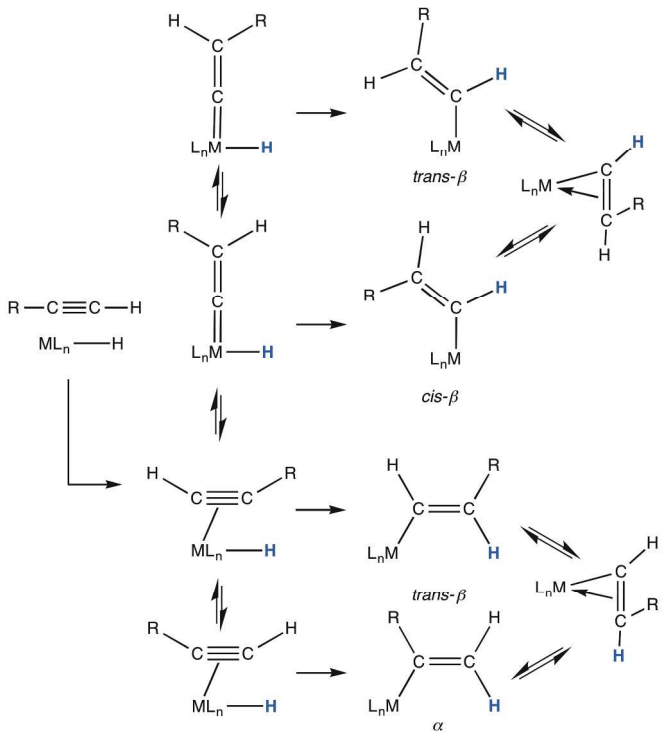


Fig. 10 Molecular structure of **20** in a crystal of **20**·Me_2CO with 50% probability displacement ellipsoids. For clarity, most hydrogen atoms and the solvent have been omitted and phenyl groups simplified. One of three crystallographically independent molecules is shown. Selected bond distances [Å] and angles [°]: Ru1–C1 2.123(8), Ru1–C8 1.856(8), P1–Ru1 2.365(2), S1–Ru1–S2 70.49(8), C1–C2 1.315(12), B1–C2–1.546(15), P2–Ru1 2.364(2), Ru1–S1 2.440(2), Ru1–S2 2.517(2), H21···S1 2.608, Ru1–C1–C2 128.6(6), B1–C2–C1 126.4(8). Inset: Possible hydrogen-bonding in the equatorial plane.

Heating a solution of **20** with excess **1** does indeed result in the clean formation of **9** and **10**, thereby substantiating its intermediacy in the formation of **9** from **1** and **7**.

On the nature of compound 14a. As noted above, a side product is observed in the formation of **14**, which would appear to also be a σ-alkenyl complex. Three possibilities are considered here, though none could be definitively confirmed. Firstly, for the hydrometallation of terminal alkynes, coordination of the alkyne followed by insertion into the metal-hydride could in principle provide two isomers with the unique substituent α- or β- to the metal. Furthermore, the possibility of σ-π alkenyl coordination provides a mechanism whereby the regiochemistry of the alkylidene unit may be reversed (Scheme 7). Because such insertion processes are typically in equilibrium with the reverse β-elimination, the system will in most cases settle down to the thermodynamic preference for a bulky substituent to be more remote from the metal and its associated ligands. Nevertheless, in the case of ethynyl benzene, it has been suggested[16a] that the alternative α-isomer [RuCl(CPh=CH_2)(CO)(PPh_3)$_2$] may form.

The large value of $^3J_{HH}$ (19.6 Hz) observed for the vinylic group of **14a** would, however, be inconsistent with geminal coupling in [Ru{C(BMIDA)=CH_2)Cl(CO)(PPh_3)$_2$] (**α-14a**). Secondly, an alternative mechanism may operate in which vinylidene formation competes with insertion, in which case migratory insertion of hydride and vinylidene ligands could produce either the *trans*-β or *cis*-β isomers. In general the latter is disfavoured unless some subsequent interaction with the metal can provide impetus, e.g., the formation of a chelate as occasionally observed for reactions of propiolic esters.[16b,25]



Scheme 7 Possible regio-isomers for terminal alkyne hydro-metallation.

Molecular modeling (MMFF) of the ***cis*-β-14a**, with or without chelation of an ester group suggests excessive steric repulsion with the co-ligands and loss of a phosphine to accommodate such steric pressures is discounted by the apparent, albeit unresolved, triplet structure of the low-field ^{1}H NMR resonance for Hα. Thus whilst we can discount some of the more obvious possibilities (Scheme 7), we remain at a loss as to the identity of **14a**.

Conclusions

The first examples of σ-alkynyl, σ-alkenyl and vinylidene ligands bearing four coordinate boron substituents have been obtained via organometallic transformations based on precedent for more conventional alkynes. In general, ethynyl-BMIDA (**1**) was found to behave much like any other terminal alkyne, without any indication of trans-annular boratrane N→B dissociation. Spectroscopic data for the various derivatives suggest that the BMIDA group is comparatively positively inductive (***+I***), in contrast to negatively mesomeric (***–M***) three-coordinate boryl substituents.

Experimental

General Considerations. All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line and inert atmosphere (argon) drybox techniques with dried and degassed solvents. NMR spectra were recorded at 25°C on a Varian Mercury 300 (^{1}H at 300.1 MHz, ^{31}P at 121.5 MHz), Varian Inova 300 (^{1}H at 299.9 MHz, ^{13}C at 75.47 MHz, ^{31}P at

121.5 MHz), Varian Mercury 400 (^{1}H at 399.9 MHz, ^{13}C at 100.5 MHz, ^{31}P at 161.9 MHz, 11B at 128.4 MHz) or Bruker Avance 600 (^{1}H at 600.0 MHz, ^{13}C at 150.9 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peak (^{1}H, ^{13}C, relative to $SiMe_4$) or external 85% H_3PO_4 (^{31}P) or $BF_3.OEt_2$ (^{11}B) with coupling constants given in Hz. t^v refers to a virtual triple resonance (indicative of *trans*-$Ru(PPh_3)_2$ geometry, with apparent coupling quoted) Infrared spectra were obtained from solution and in the solid state (KBr pellets) using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental microanalytical data were obtained from the ANU Research School of Chemistry microanalytical service. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. Data for X-ray crystallography were collected with Nonius Kappa (Mo) or Agilent Super Nova (Mo, Cu) CCD diffractometer. The compounds $[Ru(CO)_2(PPh_3)_3]$,[7b] $[Ru(C_2H_4)(CO)_2(PPh_3)_2]$,[7] $[RuCl(dppe)_2]PF_6$[14] and $[RuHCl(CO)(PPh_3)_3]$[15] were prepared according to published procedures. The compounds $[RuH(S_2CNR_2)(CO)(PPh_3)_2]$ (R = Me, Et) were prepared by treating $[RuHCl(CO)(PPh_3)_3]$ with $Na[S_2CNMe_2]$ or $[Et_2NH_2][S_2CNEt_2]$.[26] All other reagents were obtained from commercial sources.

Synthesis of [RuH(C≡CBMIDA)(CO)$_2$(PPh$_3$)$_2$] (4): *Method 1:* A suspension of $[Ru(C_2H_4)(CO)_2(PPh_3)_2]$ (0.071 g, 0.1 mmol) and **1** (0.018 g, 0.1 mmol) in dichloromethane (2 mL) was stirred for 15 min during which time the yellow solution turned colourless. All volatiles were removed under high vacuum to leave a colourless solid. The residue was recrystallised from a mixture of CH_2Cl_2 and pentane at -15°C over 72 h to provide X-ray diffraction quality colourless crystals of two different habits. Yield: 0.086 g (0.10 mmol, 100%). *Method 2:* A suspension of $[Ru(CO)_2(PPh_3)_3]$ (0.053 g, 0.06 mmol) and **1** (0.010 g, 0.06 mmol) in dichloromethane (2 mL) was stirred for 15 min. The colourless solution that formed was freed of volatiles and the residue crystallized from a mixture of CH_2Cl_2 and pentane. Yield 0.045 g (0.052 mmol, 52%). NMR (CD_2Cl_2, 25°C): ^{1}H: δ_H = –5.87 (t, $^2J_{PH}$ 20, 1 H, RuH), 1.80 (s, 3 H, CH_3), 2.77 (d, $^2J_{HH}$ 16.2, 2 H, CH_2), 3.21 (d, $^2J_{HH}$ 16 Hz, 2 H, CH_2), 7.35-7.77 (m, 30 H, C_6H_5); ^{11}B{^{1}H}: δ_B = 4.7; ^{31}P{^{1}H}: δ_P = 44.95 (d, $^2J_{PH}$ 4.5 Hz). Acc. Mass: Found: *m/z* = 902.0953. Calcd. for $C_{45}H_{38}{}^{11}BKNO_6P_2{}^{102}Ru$ 902.0948 $[M + K]^+$. IR (DCM): ν_{CO} 1773, 1988, 2032, 2081 (ν_{CC}) cm^{-1}. Satisfactory elemental microanalytical data were not obtained due to the reversible loss of HC≡CBMIDA during various recrystallization attempts. *Crystal data*: $C_{45}H_{38}BNO_6P_2Ru.0.3(CH_2Cl_2)$, M_r = 888.11, T = 200(2) K, triclinic, space group *P*-1 (No.2), a = 12.2088(3), b = 19.7555(4), c = 21.8833(5) Å, α = 64.8712(13), β = 79.6801(12), γ = 89.3128(15)°, V = 4689.03(19) Å^3, Z = 4, D_{calcd} = 1.258 Mgm^{-3}, μ(Mo Kα) 0.48 mm^{-1}, colourless prism, 0.05 × 0.09 × 0.32 mm, 56,843 measured reflections with $2\theta_{max}$ = 50.0°, 16,497 independent reflections, 16,489 adsorption-corrected data used in F^2 refinement, 1036 parameters, 0 restraints, R_1 = 0.070, wR_2 = 0.210 for 10,632 reflections with $I > 2\sigma(I)$, CCDC 1037265. *Crystal data*: $C_{45}H_{38}BNO_6P_2Ru$, M_r = 862.63, T = 200(2) K, triclinic, space group *P*-1 (No.2), a = 12.2188(4), b = 18.0463(5), c = 21.6354(4) Å, α = 107.8448(17), β = 94.2812(15), γ = 100.3671(14)°, V = 4423.9(2) Å^3, Z = 4, D_{calcd} = 1.295 Mgm^{-3}, μ(Mo Kα) 0.47 mm^{-1}, colourless block, 0.08 × 0.12 × 0.17 mm, 55,677 measured reflections with $2\theta_{max}$ = 50.2°, 15,711 independent reflections, 15,704 absorption-corrected data used in F^2 refinement, 1,233 parameters, 502 restraints, R_1 = 0.049, wR_2 = 0.115 for 10,192 reflections with $I > 2\sigma(I)$, CCDC 1037266.

Synthesis of [RuCl(C≡CBMIDA)(CO)$_2$(PPh$_3$)$_2$] (5): A suspension of $[Ru(CO)_2(PPh_3)_3]$ (0.094 g, 0.10 mmol) and **1** (0.018 g, 0.1 mmol) in chloroform (9 mL) was stirred for 2 h. Initially upon partial dissolution a yellow colour developed, but rapidly decolourised after ~1 min of stirring. Petroleum ether 60-80°C (~10 mL) was added to fully precipitate a beige solid that was collected on a sinter, then washed with pet. ether 60-80°C (~4 mL) and EtOH (~10 mL) and dried in vacuo. The product as found to be only sparingly soluble in most common solvents. Yield: 0.030 g (0.033 mmol, 33%). NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 3.08 (d, $^4J_{HH}$ 3.6, 3 H, CH_3), 3.73 (dd, $^2J_{HH}/^4J_{HH}$ 16.4/3.8, 2 H, CH_2), 3.80 (dd, $^2J_{HH}/^4J_{HH}$ 16.4/4.0 Hz, 2 H, CH_2), 7.39 (m, 18 H, C_6H_5), 7.92 (m, 12 H, C_6H_5); ^{11}B{^{1}H}: δ_B = 5.5; ^{31}P{^{1}H}: δ_P = 17.73. ESI-MS (+ve ion): *m/z* = ESI-MS (+ve ion): *m/z* = 836.2 $[HM-Cl-CO]^+$, 807.1 $[HM-Cl-CO]^+$. IR (DCM): ν_{CO} 1775, 1995, 2058, 2080 (ν_{CC}) cm^{-1}; IR (KBr Plate): ν_{CO} 1775, 1992, 2056, 2082 (ν_{CC}) cm^{-1}.

Synthesis of [Ru(C≡CBMIDA)(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$] (8): A solution of $[Ru(H)(S_2CNMe_2)(CO)(PPh_3)_2]$ (**6**: 0.194 g, 0.25 mmol) and **1** (0.045 g, 0.25 mmol) was heated to reflux for 16 hours. All volatiles were removed under high vacuum and further **1** (0.045 g, 0.25 mmol) was added followed by THF (16 mL). The mixture was heated under reflux for 16 hours then allowed to cool and diluted with hexane (~16 mL). Slow concentration under vacuum to ca 15 mL afforded a yellow precipitate that was isolated by filtration, washed with hexane (~100 mL) and then Et_2O (~200 mL). The resulting yellow solid was extracted with benzene extracted with benzene to leave a white solid (**10**: H_2C=CHBMIDA) on the sinter. All volatiles were removed from the benzene extract on a rotary evaporator and residue was recrystallised from a mixture of CH_2Cl_2 and pentane to a a pale yellow solid. Yellow X-ray diffraction quality crystals were obtained by evaporation of an acetone solution. Yield: 0.056 g (0.059 mmol, 23%). NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 2.27 (s, 3H, $BNCH_3$), 2.49 (s, 3H, NCH_3), 2.71 (s, 3H, NCH_3), 3.20 (d, $^2J_{HH}$ 16.0 Hz, 2H, CH_2), 3.42 (d, $^2J_{HH}$ 16.0 Hz, 2H, CH_2), 7.32 (m, 18H, C_6H_5), 7.84 (m, 12H, C_6H_5); ^{11}B{^{1}H}: δ_B = 10.1 (br); ^{13}C{^{1}H}: δ_C = 46.58 (NCH_2), 61.02 ($BNCH_3$), 61.44 [$N(CH_3)_2$], 127.4 [$C^{2,6}(C_6H_5)$], 129.4 [$C^4(C_6H_5)$], 133.8 [t^v, J_{CP} 21.9 Hz, $C^1(C_6H_5)$], 135.1 [$C^{3,5}(C_6H_5)$], 138.4 (C≡*C*B), 144.9 (RuC), 167.8 (CO_2); ^{31}P{^{1}H}: δ_P = 39.49. ESI-MS (+ve ion): *m/z* = 955.2 $[M + H]^+$, 815.1 $[M + NCMe]^+$, 744.1 $[M-CH=CHBMIDA]^+$. IR (DCM): ν_{CO} 1765, 1943, 2057 (ν_{CC}) cm^{-1}; IR (KBr Plate): ν_{CO} 1763, 1938, 2060 (ν_{CC}) cm^{-1}. *Crystal data*: $C_{47}H_{43}BN_2O_5P_2RuS_2$, M_r = 953.83, T = 150(2) K, monoclinic, space group *Pc*, a = 10.6884(1), b = 10.9013(1), c = 18.7310(1) Å, β = 91.4444(6)°,

V = 2181.80(3) Å^3, Z = 2, D_{calcd} = 1.452 Mgm^{-3}, μ(Cu Kα) 4.89 mm^{-1}, yellow block, 0.06 × 0.10 × 0.12 mm, 42,228 measured reflections with $2\theta_{max}$ = 144.8°, 7,220 independent reflections, 7,192 absorption-corrected data used in F^2 refinement, 542 parameters, 2 restraints, R_1 = 0.026, wR_2 = 0.070 for 7088 reflections with $I > 2\sigma(I)$, CCDC 1037267.

Synthesis of [Ru(C≡CBMIDA)(S_2CNEt_2)(CO)(PPh_3)$_2$ (9)]: A solution of [RuH(S_2CNEt_2)(CO)(PPh_3)$_2$] (**6**: 0.401 g, 0.50 mmol) and **1** (0.181 g, 1.0 mmol) in CH_2Cl_2 (35 mL) was heated under reflux for 36 h to provide a yellow solution. All volatiles were removed and the residue then was extracted with benzene (~100 mL) to give a yellow solution and a colourless solid (H_2C=CHBMIDA) that was collected by filtration. The benzene was removed from the extract in vacuo and the residue recrystallised from a mixture of CH_2Cl_2 and hexane to give a yellow precipitate that was isolated by filtration, washed with hexane (~100 mL) and dried in vacuo. Yellow X-ray diffraction quality crystals were obtained by solvent diffusion of pentane into a solution of **9** in CH_2Cl_2. Yield: 0.310 g (0.316 mmol, 63%). NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 0.56 (t, $^3J_{HH}$ 8.0, 3 H, NCH_2CH_3), 0.74 (t, $^3J_{HH}$ 8.0, 3 H, NCH_2CH_3), 2.24 (s, 3 H, NCH_3), 2.75 (q, $^3J_{HH}$ 7.2, 2 H, NCH_2CH_3), 2.99 (q, $^3J_{HH}$ 7.2, 2 H, NCH_2CH_3), 3.17 (d, $^2J_{HH}$ 16.0, 2 H, CH_2), 3.38 (d, $^2J_{HH}$ 16.0 Hz, 2H, CH_2), 7.32 (m, 18H, C_6H_5), 7.81 (m, 12H, C_6H_5); ^{11}B{^{1}H}: δ_B = 10.3 (br); ^{31}P{^{1}H}: δ_P = 39.53. Acc. Mass: Found: *m/z* = 982.1509. Calcd. for $C_{49}H_{47}{}^{11}BN_2O_5P_2{}^{102}RuS_2$ 982.1538 [M]$^+$. ESI-MS(+ve ion): *m/z* = 843.1 [M + NCMe - CH=CHBMIDA]$^+$, 802.1 [M - CH=CHBMIDA]$^+$. IR (DCM): ν_{CO} 1762, 1945, 2062 (ν_{CC}) cm^{-1}; IR (KBr Plate): ν_{CO} 1759, 1936, 2059 (ν_{CC}) cm^{-1}. *Crystal data*: $C_{49}H_{47}BN_2O_5P_2RuS_2.0.5CH_2Cl_2$, M_r = 2048.70, T = 150(2) K, triclinic, space group *P*-1 (No.2), a = 11.89073(17), b = 18.5016(3), c = 23.4234(4) Å, α = 101.8728(15), β = 91.4641(13), γ = 105.6931(14)°, V = 4836.81(14) Å^3, Z = 2, D_{calcd} = 1.407 Mgm^{-3}, μ(Cu Kα) 4.95 mm^{-1}, yellow plate, 0.05 × 0.14 × 0.19 mm, 28,693 measured reflections with $2\theta_{max}$ = 144.6°, 18,370 independent reflections, 15,813 absorption-corrected data used in F^2 refinement, 1,144 parameters, 1 restraint, R_1 = 0.046, wR_2 = 0.111 for 13,765 reflections with $I > 2\sigma(I)$, CCDC 1037268.

Isolation of H_2C=CHBMIDA (10):[2j] Crudely isolated as a white powder that remains on the sinter after the benzene extraction of Ru(C≡CBMIDA)(S_2CNEt_2)(CO)(PPh_3)$_2$. Colourless X-ray diffraction quality crystals were obtained by solvent diffusion of DCM/pentane. Yield: 0.065 g (0.36 mmol, 71%). NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 2.67 (dd, *trans*-$^3J_{HH}$/*cis*-$^3J_{HH}$ 12.0/8.0, 1 H, H_2C=C*H*B), 2.71 (s, 3 H, CH_3), 3.68 (d, $^2J_{HH}$ 16.4, 2 H, CH_2), 3.74 (m, 1 H, *cis*-H_2C=CHB), 3.79 (d, $^3J_{HH}$ 13.6, 1 H, *trans*-H_2C=CHB), 3.82 (d, $^2J_{HH}$ 16.0 Hz, 2 H, CH_2); ^{11}B{^{1}H}: δ_B = 5.3 (br). C*rystal data*: $C_7H_{10}BNO_4$, M_r = 182.97, T = 150(2) K, monoclinic, space group $P2_1/n$, a = 6.1164(2), b = 11.9985(4), c = 11.6778(3) Å, β = 90.951(3)°, V = 856.89(5) Å^3, Z = 4, D_{calcd} = 1.418 Mgm^{-3}, μ(Cu Kα) = 0.97 mm^{-1}, colourless plate, 0.02 × 0.18 × 0.34 mm, 7,522 measured reflections with $2\theta_{max}$ = 144.6°, 1,692 independent reflections, 1,684 absorption-corrected data used in F^2 refinement, 118 parameters, 0 restraints, R_1 = 0.046, wR_2 = 0.117 for 1,560 reflections with $I > 2\sigma(I)$.

Synthesis of [RuCl(=C=CHBMIDA)(dppe)$_2$][PF_6] ([11]PF_6): A suspension of [RuCl(dppe)$_2$][PF_6] (0.04 g, 0.037 mmol) and acetylene BMIDA (0.007 g, 0.039 mmol) in dichloromethane (4 mL) was sonicated for 30 min (cleaning bath), then stirred for 3 days during which time the reagents dissolved. All volatiles were removed under high vacuum to leave a light red solid which was recrystallised from a mixture of CH_2Cl_2 and pentane to provide a pale orange/red microcrystalline coloured solid. Recrystallisation in DCM/pentane over 72 h produced X-ray diffraction quality pale orange crystals. Yield: 0.033 g (0.026 mmol, 71%). Anal. Found: C, 54.24; H, 4.47: N, 1.23%. Calcd. for $C_{59}H_{56}BClF_6NO_4P_5Ru.CH_2Cl_2$: C, 53.61; H, 4.35; N, 1.04%. NB: The sample used for microanalysis was stored under high vacuum which would appear to have resulted in partial desolvation given that the data are more consistent with ¾(CH_2Cl_2) *cf.* the crystallographically established monosolvate: Calcd for $C_{59}H_{56}BClF_6NO_4P_5Ru.0.75(CH_2Cl_2)$: C, 54.24; H, 4.38; N, 1.06%. NMR (CD_2Cl_2, 25°C): ^{1}H: δ_H = 2.01 (s.br, 3 H, CH_3), 2.74 (m.br, 4 H, PCH_2), 2.98 (m.br, 4 H, PCH_2), 3.08 (s, 1 H, C=CH), 3.33 (m.br, 2 H, NCH_2), 3.75 (m.br, 2 H, NCH_2), 6.99-7.51 (m, 40 H, C_6H_5); ^{11}B{^{1}H}: δ_B = 6.7; ^{13}C{^{1}H}: δ_C = 29.16 (m, PCH_2), 29.96 (m, PCH_2), 46.27 (NCH_3), 61.60 (NCH_2), 93.0 (v.br., Cβ) 127.98 (C_6H_5), 128.21 (C_6H_5), 128.77 (s, C_6H_5), 129.12 (s, C_6H_5), 130.59 (s, C_6H_5), 131.00 (s, C_6H_5), 131.59 [d, $^1J_{CP}$ 55.7 Hz, $C^1(C_6H_5)$], 133.24 (s, C_6H_5), 134.13 [d, $^1J_{CP}$ 61.2 Hz, $C^1(C_6H_5)$], 134.16 (s, C_6H_5), 166.76 [s, OC(O)], 334.7 (pent., $^2J_{PC}$ = 10.2 Hz, Ru=C), the resonance for Cβ could not be unambiguously identified; ^{31}P{^{1}H}: δ_P = –143.81 (sept, $^1J_{PF}$ 711.1 Hz, PF_6), 45.45 (dppe). ESI-MS (+ve ion): *m/z* = 1119.2 [M + NCMe - Cl – H]$^+$, 899.1 [M - Cl - C=CHBMIDA]+. *Crystal data*: [$C_{59}H_{56}BClNO_4P_4Ru$]-[PF_6].CH_2Cl_2, M_r = 1344.22, T = 200(2) K, triclinic, space group *P*-1 (No.2), a = 13.1367(8), b = 14.1164(8), c = 16.2360(7) Å, α = 86.068(3), β = 73.777(3), γ = 87.542(3)°, V = 2883.3(3) Å^3, Z = 2, D_{calcd} = 1.548 Mgm^{-3}, μ(Mo Kα) 0.62 mm^{-1}, pale yellow plate, 0.05 × 0.10 × 0.17 mm, 41,835 measured reflections with $2\theta_{max}$ = 50.2°, 10,207 independent reflections, 10,204 absorption-corrected data used in F^2 refinement, 730 parameters, 0 restraint, R_1 = 0.058, wR_2 = 0.148 for 6,573 reflections with $I > 2\sigma(I)$, CCDC 1037270.

Synthesis of [RuCl(C≡CBMIDA)(dppe)$_2$] (12): To a red solution of [RuCl(=C=CHBMIDA)(dppe)$_2$][PF_6] (**11**: 0.033 g, 0.026 mmol) in dichloromethane (4 mL) was added a large excess of NEt_3 (~0.1 mL, 0.04 mmol). The mixture was stirred for 1 h, during which time the solution decolourised to yellow. The resulting suspension was then to settle for 30 min to give a yellow coloured precipitate that was isolated by cannula filtration. The yellow solid was washed with DCM (2 mL) and dried under vacuum for 30 min. The compound was found to have poor solubility in common solvents, which prevented satisfactory ^{1}H NMR and ^{13}C{^{1}H} NMR spectra from being obtained. Yield: 0.017 g (0.015 mmol, 59%). Anal. Found: C, 60.41; H, 4.71: N, 1.44%. Calcd for

$C_{59}H_{55}BClNO_4P_4Ru.CH_2Cl_2$: C, 60.14; H, 4.79; N, 1.70%. NMR ($CDCl_3$, 25°C): $^{11}B\{^1H\}$: δ_B = 5.4 (s); $^{31}P\{^1H\}$: δ_P = 47.80 (s). ESI-MS (+ve ion): *m/z* = 1119.3 [M-Cl+NCMe]$^+$, 957.2 M-BMIDA]$^+$. Acc. Mass: Found: m/z = 1119.2493; Calcd. for $C_{61}H_{58}{}^{11}BN_2O_4P_4{}^{102}Ru$ 1119.2484. IR (DCM): ν_{CO} 1745, 1773, 2023 (ν_{CC}) cm^{-1}; IR (KBr Plate): ν_{CO} 1750, 2024 (ν_{CC}) cm^{-1}.

Synthesis of [RuCl(CH=CHBMIDA)(CO)(PPh$_3$)$_2$] (14): Method 1: A suspension of [RuHCl(CO)(PPh_3)$_3$] (**13**: 0.20 g, 0.21 mmol) and **1** (0.04 g, 0.22 mmol) in CH_2Cl_2 (10 mL) was stirred for 30 min during which time the pale pink suspension dissolved to afford a brown solution. The product was precipitated from solution by dilution with hexane (60 mL) to give a mustard coloured solid which was recrystallised from a mixture of dichloromethane and diethyl ether. The microcystalline solid was isolated by cannula filtration, washed with diethyl ether and dried in vacuo. Yield: 0.078 g (0.09 mmol, 42%). Method 2: A suspension of [RuHCl(CO)(PPh_3)$_3$] (**13**: 8.20 g, 8.61 mmol) and **1** (1.56 g, 8.62 mmol) in CH_2Cl_2 (400 mL) was stirred for 45 min. Dilution with petroleum ether 40-60°C (1.5 L) provided a mustard coloured solid that was left to settle overnight. The precipitate was isolated by filtration and washed with Et_2O (200 mL). The residue was then redissolved in DCM (600 mL) and re-precipitated by dilution with Et_2O (3.25 L). The precipitate was isolated by filtration and dried in vacuo. Yield: 0.995 g (1.14 mmol, 13%). NMR (d_8-THF, 25 °C): ^1H: δ_H = 2.16 (s, 3 H, NCH_3), 3.16, 3.69 (d x 2, 4 H, $^2J_{HH}$ = 16.5, NCH_2), 5.10 (dt, 1 H, $^3J_{HH}$ = 12.9, $^4J_{PH}$ = 2.1, =CHB), 7.30 – 7.45, 7.59 (m x 2, 30 H, C_6H_5), 8.10 (d, 1 H, $^3J_{HH}$ = 12.9 Hz, RuCH). $^{13}C\{^1H\}$: δ_C = 47.82 (NCH_3), 61.61 (NCH_2), 129.0 [t^v, J_{PC} = 4.9, $C^{3,5}(C_6H_5)$], 130.8 [$C^4(C_6H_5)$], 132.3, 132.8 (=CHB, assignment equivocal), 133.6 [t^v, J_{PC} = 21.5, $C^1(C_6H_5)$,], 135.3 [t^v, J_{PC} = 5.9 Hz], 168.1 (CO_2), 177.7 (identified by HSQC, RuCH), RuCO not identified due to poor solubility. $^{11}B\{^1H\}$: δ_B = 5.8. $^{31}P\{^1H\}$: δ_P= 30.70. NMR ($CDCl_3$, 25 °C): ^1H: δ_H = 2.09 (s, 3 H, NCH_3), 3.26, 3.44 (d x 2, 4 H, $^2J_{HH}$ = 16.0, NCH_2), 5.09 (s, 1 H, $^3J_{HH}$ = 13.2, =CHB), 7.00 – 7.74 (m x 6, 30 H, C_6H_5), 8.57 (d, 1 H, $^3J_{HH}$ = 13.2 Hz, RuCH). $^{11}B\{^1H\}$: δ_B = 4.8. $^{31}P\{^1H\}$: δ_P= 32.10. IR (CH_2Cl_2): 1930 ν_{CO}, 1774 ν_{CO2} cm^{-1}. IR (KBr Plate): 1921 ν_{CO}, 1743, 1766 ν_{CO2} cm^{-1}. Anal. Found: C, 58.75; H, 4.53; N, 1.84%. Calcd. for $C_{44}H_{39}BClNO_5P_2Ru.0.5(CH_2Cl_2)$: C, 58.51; H, 4.41; N, 1.53% Acc. Mass: Found: *m/z* = 877.1711. Calcd. for $C_{46}H_{42}{}^{11}BN_2O_5P_2{}^{102}Ru$ 877.1706 [M-Cl+NCMe]$^+$. ESI-MS(=ve ion): *m/z* = 877.3 [M-Cl+NCMe]$^+$, 836.3 [M-Cl]$^+$, 737.3 [Ru(CO)(NCMe)$_2$(PPh_3)$_2$]$^+$, 696.3 [Ru(CO)(NCMe)(PPh_3)$_2$]$^+$, 655.3 [Ru(CO)(PPh_3)$_2$]$^+$.

Prior to recrystallisation, a second minor isomer (**14a**) was observed as a contaminant, which could be removed but not isolated. Data for '**14a**': NMR ($CDCl_3$, 25 °C): ^1H: δ_H = 2.11 (s, 3 H, NCH_3), 3.02, 3.46 (d x 2, 4 H, partially obscured by major isomer), 5.51 (d, $^3J_{HH}$ 19.2 Hz, 1 H, =C*H*B), 8.28 (d, $^3J_{HH}$ 19.6 Hz, 1H, RuC*H*). $^{31}P\{^1H\}$: δ_P = 22.71 (s). All attempts to obtain crystallographic grade crystals of **14** met with failure, though on one occasion traces of an unexpected decomposition product were obtained from chloroform under aerobic conditions and structurally identified as the 2-chloroacrylato complex [Ru(O_2CCH=CHCl)Cl(CO)(PPh_3)$_2$] (**21**, Figure 11). Insufficient of this complex was obtained for spectroscopic characterization and mechanistic conjecture is suitably restrained, but most likely involves (radical) cleavage of the C–BMIDA bond and insertion of extraneous atmospheric CO_2 into the Ru–C bond. Crystal data (Figure 11): $C_{40}H_{32.2}Cl_{1.8}O_3P_2Ru$, M_r = 787.73, T = 200(2) K, monoclinic, space group $C2/c$, a = 17.0407(5), b = 11.2086(3), c = 19.6906(5) Å, β = 103.4013(14)°, V = 3658.54(17) Å^3, Z = 4, D_{calcd} = 1.430 Mgm^{-3}, μ(Mo Kα) 0.68 mm^{-1}, yellow lath, 0.05 × 0.10 × 0.45 mm, 38624 measured reflections with $2\theta_{max}$ = 55.0°, 4212 independent reflections, 4210 absorption-corrected data used in F^2 refinement, 245 parameters, 0 restraints, R_1 = 0.047, wR_2 = 0.097 for 2306 reflections with $I > 2\sigma(I)$, CCDC 1037272.

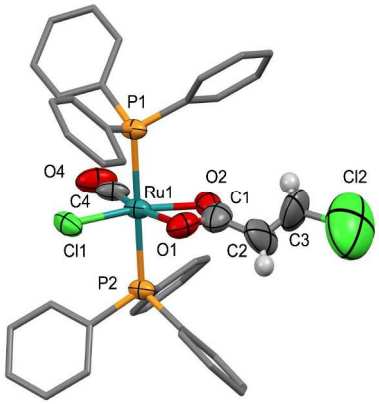


Fig. 11 Molecular structure of **21** from crystals obtained by aerial decomposition product of **14.** Depicted with 50% probability displacement ellipsoids. For clarity, most hydrogen atoms have been omitted and phenyl groups simplified.

Synthesis of [Ru(CH=CHBMIDA)Cl(CO)$_2$(PPh$_3$)$_2$] (16): Carbon monoxide was bubbled through a suspension of [Ru(CH=CHBMIDA)Cl(CO)(PPh_3)$_2$] (**14**: 0.052 g, 0.06 mmol) for approximately 5 min. during which time the supernatant darkened. A colourless precipitate formed over the 1 h, which was allowed to settle, then separated by cannula filtration, washed with hexane (2 × 4 mL) and dried in vacuo. The product was found to possess very poor solubility in common solvents, which compromised subsequent analyses. Yield: 0.019 g (0.021 mmol, 35%). Anal. Found: C, 59.73; H, 4.39: N, 1.68%. Calcd for $C_{45}H_{39}BClNO_6P_2Ru$: C, 60.12; H, 4.37; N, 1.56%. NMR ($CDCl_3$, 25°C): ^1H: δ_H = 2.11 (s, 3 H, CH_3), 3.04 (d, $^2J_{HH}$ 16.0, 2 H, CH_2), 3.40 (d, $^2J_{HH}$ 16.0, 2 H, CH_2), 5.57 (d, $^3J_{HH}$ 19.6, 1 H, =C*H*B), 7.39 (m, 18 H, C_6H_5), 7.74 (m, 12 H, C_6H_5), 8.29 (d, $^3J_{HH}$ 19.6 Hz, 1 H, RuC*H*); $^{31}P\{^1H\}$: δ_P = 22.49. Acc. Mass: Found: *m/z* = 905.1643. Calcd. for $C_{47}H_{42}{}^{11}BKN_2O_6P_2{}^{102}Ru$ 905.1655 [M+NCMe-Cl]$^+$. ESI-MS(+ve ion): *m/z* = 877.2 [M+NCMe-Cl-CO]$^+$. IR (DCM): ν_{CO} 1763, 1974, 2037 cm^{-1}; IR (KBr Plate): ν_{CO} 1762, 1966, 2032 cm^{-1}. Crystals, albeit of low quality, suitable for X-ray diffraction analysis were obtained by slow diffusion of head space CO into an undisturbed CH_2Cl_2 solution of **14** in a

narrow (NMR) tube. The best crystal chosen diffracted poorly such that insufficient data were acquired to allow full anisotropic refinement of all atomic positions. The study nevertheless confirmed the geometry. Crystal data: $C_{45}H_{39}BClNO_6P_2Ru$, M_r = 899.09, T = 150(2) K, triclinic, space group P-1 (No. 2), a = 10.1224(5), b = 17.350(1), c = 26.591(3) Å, α = 88.449(7), β = 89.008(6), γ = 83.422(5)°, V = 4637.0(6) Å^3, Z = 4, D_{calcd} = 1.288 Mgm^{-3}, μ(Cu Kα) 4.279 mm^{-1}, colourless lath, 0.017 × 0.050 × 0.303 mm, 17,677 measured reflections with $2\theta_{max}$ = 144°, 17,182 independent absorption-corrected reflections used in F^2 refinement, 457 parameters, 0 restraints, R_1 = 0.205, wR_2 = 0.419 for 11,171 reflections with $I > 2\sigma(I)$.

Synthesis of [Ru(CH=CHBMIDA)Cl(CNMes)(CO)(PPh$_3$)$_2$] (17): A suspension of [Ru(CH=CHBMIDA)Cl(CO)(PPh$_3$)$_2$] (0.052 g, 0.06 mmol) and $CNC_6H_2Me_3$-2,4,6 (CNMes: 0.009 g, 0.06 mmol) in dichloromethane (2 mL) was stirred for 8 h following the immediate formation of a dark solution upon dissolution. The mixture was layered with hexane, slow diffusion of which afforded a brown solid that was isolated by cannula filtration, washed with hexane and dried in vacuo. Yield: 0.049 g (0.048 mmol, 80%). Anal. Found: C, 63.48; H, 4.99: N, 2.89%. Calcd for $C_{54}H_{50}BClN_2O_5P_2Ru$: C, 63.82; H, 4.96; N, 2.76%. NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 1.96 (s, 6 H, CCH_3-2,6), 2.09 (s, 3 H, NCH_3), 2.25 (s, 3 H, CCH_3-4), 3.02 (d, $^2J_{HH}$ 16.0, 2 H, CH_2), 3.37 (d, $^2J_{HH}$ 16.0, 2 H, CH_2), 5.69 (d, $^3J_{HH}$ 20.0 Hz, 1 H, =C*H*B), 6.74 (s, 2 H, C_6H_2), 7.27 (m, 18 H, C_6H_5), 7.59-7.62 (m, 12 H, C_6H_5), 8.59 (dt, $^3J_{HH}$ = 20.0, $^3J_{PH}$ 2.6 Hz, 1 H, RuCH); ^{11}B{^{1}H}: δ_B = 10.7 (br); ^{13}C{^{1}H}: δ_C = 18.45 [Me^{2,6}($C_6H_2Me_3$)], 21.24 [Me^4 ($C_6H_2Me_3$)], 45.68 (NMe), 61.27 (NCH_2), 125.3 (CHB), 127.9 [t^v, J_{CP} 4.5, C^{2,6}(C_6H_5)], 128.3 [t, $^1J_{CP}$ 28.7, C^1(C_6H_5)], 129.7 [C^4(C_6H_5)], 131.2 ($C_6H_2Me_3$), 133.6 [t, J_{PC} 5.1, C^1($C_6H_2Me_3$)], 133.9 ($C_6H_2Me_3$), 134.4 [d, J_{CP} 4.0 Hz, C^{3,5}(C_6H_5)],138.0 [C^4($C_6H_2Me_3$)], 168.8 [OC(O)], 182.1 [t, $^2J_{CP}$ 13.8 Hz, RuCN], 200.8 (RuCO), RuCα not be definitively assigned due to overlapping resonances; ^{31}P{^{1}H}: δ_P = 24.87. Acc. Mass: Found: *m/z* = 1022.2598. Calcd. for $C_{56}H_{53}{}^{11}BKN_3O_5P_2{}^{102}Ru$ 1022.2597 [M+K+NCMe-Cl]$^+$. ESI-MS (+ve ion): *m/z* = 1271.4 [M+2(CNMes)-Cl]$^+$, 1126.3 [M+CNMes-Cl]$^+$, 981.2 [M – Cl]$^+$ (indicative of CNMes scrambling under MS conditions). IR (DCM): ν_{CO} 1762, 1959, 2118 (ν_{CN}) cm^{-1}; IR (KBr Plate): ν_{CO} 1762, 1952, 2117 (ν_{CN}) cm^{-1}.

Synthesis of [Ru(CH=CHBMIDA)(CO)(PPh$_3$){HB(pz)$_3$}] (18) Method 1: A suspension of [Ru(CH=CHBMIDA)Cl(CO)(PPh$_3$)$_2$] (**14**: 0.052 g, 0.06 mmol) and K[HB(pz)$_3$] (0.015 g, 0.06 mmol) in dichloromethane (2 mL) was stirred for 15 min, following the immediate formation of a green/brown solution. Hexane (2 mL) was added to precipitate the KCl and the mixture stirred for 15 min before filtration through a plug (~1 cm) of diatomaceous earth to provide a pale-green filtrate. The volatiles were removed under reduced pressure to afford a pale green solid that was washed with hexane (2 x 10 mL) and dried in vacuo. Yield = 0.040 g (0.04 mmol, 64%). The compound could not be obtained in pure form due to slow decomposition in solution. **Method 2:** A suspension of [RuHCl(CO)(PPh$_3$)$_3$] (**13**: 0.381 g, 0.4 mmol) and acetylene BMIDA (**1**: 0.080 g, 0.44 mmol) in dichloromethane (20 mL) was stirred for 30 min to afford a dark brown solution. To this was added K[HB(pz)$_3$] (0.121 g, 0.48 mmol) and the mixture stirred for 30 min to give a green solution which was then filtered through a plug (~12 cm) of diatomaceous earth and freed of all volatiles under reduced pressure to provide a pale green solid. Recrystallisation from a mixture of CH_2Cl_2 and petroleum ether (b.p. 60-80°C) afforded an off-white precipitate microcrystalline solid which was collected on a glass sinter and washed with additional petroleum ether 60-80°C. The solid was extracted with with benzene (2 x 5 mL) and the combined extracts freed of volatiles to leave an off-white solid. Yield: 0.087 g (0.11 mmol, 28%). Attempts to purify the compound by recrystallisation resulted in decomposition to **1** and [RuH(CO)(PPh$_3$){HB(pz)$_3$}][23] in solution (benzene, acetone) which was complete within 24 h. NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 2.61 (s, 3 H, CH_3), 3.53-3.66 (m, 4 H, CH_2), 5.29 (d, $^3J_{HH}$ 6.8, 1 H, $C_3H_3N_2$), 5.78 (dd, $^3J_{HH}$ = 18.8, $^4J_{PH}$ = 6.4, 1 H, =CHB), 5.84, 5.89, 6.05, 6.68, 6.79 (d x 4, $^3J_{HH}$ 4 - 6 Hz, 1 H x 5, $C_3H_3N_2$), 7.08-7.10 (m, 6 H, C_6H_5), 7.24 (m, 6 H, C_6H_5), 7.34 (m, 3 H, C_6H_5), 7.54-7.67 (m, 3 H, $C_3H_3N_2$), 8.55 (dd, $^3J_{PH}$ = 18.6, $^3J_{HH}$ = 4.6 Hz, 1 H, RuCH); ^{11}B{^{1}H}: δ_B = -3.9 (HB), 5.50 (BMIDA); ^{31}P{^{1}H}: δ_P = 49.74. Acc. Mass: Found: *m/z* = 646.1227. Calcd. for $C_{30}H_{28}{}^{11}BN_7OP^{102}Ru$ 646.1230 [M+NCMe-CH=CHBMIDA]$^+$. ESI-MS(+ve ion): *m/z* = 867.2 [M+PPh$_3$-CH=CHBMIDA]$^+$, 764.2, 737.1, 696.1. IR (DCM): ν_{CO} 1770, 1939 cm^{-1}. An intermediate (**19**) was observed 30 min. after mixing that disappears as **18** forms. This was formulated as the complex [Ru(CH=CHBMIDA)(CO)-(PPh$_3$)$_2${κ^2-HB(pz)$_3$}] (**19**): NMR ($CDCl_3$, 25°C): ^{31}P{^{1}H}: δ_P = 42.57, 47.03 (**AB**, $^2J_{AB}$ 306.5 Hz). An anaerobic solution of **18** in $CDCl_3$ was observed to decompose completely over a period of 24 h to afford [RuH(CO)(PPh$_3$){HB(pz)$_3$}][23] and **1**. Data for **HC≡CBMIDA**:[27] NMR ($CDCl_3$, 25°C): ^{1}H: δ_H = 2.49 (s, 1 H, ≡CH), 3.11 (s, 3 H, NCH_3), 3.79 (s, 4 H, CH_2); ^{11}B{^{1}H}: δ_B = 5.5. ESI-MS (+ve ion): *m/z* = 566.1 [3M+Na]$^+$, 385.0 [2M+Na]$^+$, 220.0 [M+K]$^+$, 204.1 [M+Na]$^+$, 182.1 [M+H]$^+$. IR (CH_2Cl_2): ν_{CO} 1774 cm^{-1}. Crystal data: $C_7H_8BNO_4$, M_r = 180.96, T = 200(2) K, monoclinic, space group $P2_1/n$, a = 6.2422(5), b = 11.9040(11), c = 11.5004(9) Å, β = 90.726(4) °, V = 854.49(12) Å^3, Z = 4, D_{calcd} = 1.407 Mgm^{-3}, μ(Mo Kα) 0.113 mm^{-1}, colourless prism, 0.05 × 0.08 × 0.20 mm, 7616 measured reflections with $2\theta_{max}$ = 50°, 1509 independent reflections, 1504 absorption-corrected data used in F^2 refinement, 119 parameters, 24 restraints, R_1 = 0.072, wR_2 = 0.159 for 807 reflections with $I > 2\sigma(I)$, CCDC 1037264.

Synthesis of [Ru(CH=CHBMIDA)(S$_2$CNEt$_2$)(CO)(PPh$_3$)$_2$] (20): A solution of [Ru(CH=CHBMIDA)Cl(CO)(PPh$_3$)$_2$] (0.052 g, 0.06 mmol) and [NH_2Et_2][S_2CNEt_2] (0.013 g, 0.06 mmol) in CH_2Cl_2 (2 mL) and MeOH (1 mL) was stirred for 10 min to afford an orange/brown solution. The product precipitated upon dilution with hexane to give a light yellow solid that was isolated by filtration and washed with MeOH (50

mL) to remove the $[Et_2NH_2]Cl$ side product. Yield: 0.026 g (0.026 mmol, 44%). Anal. Found: C, 59.42; H, 5.02: N, 2.96%. Calcd. for $C_{49}H_{49}BN_2O_5P_2RuS_2$: C, 59.82; H, 5.02; N, 2.85%. NMR ($CDCl_3$, 25°C): ^1H: δ_H = 0.57 (t, $^3J_{HH}$ 6.8, 3 H, CH_2CH_3), 0.74 (t, $^3J_{HH}$ 6.8, 3H, CH_2CH_3), 2.03 (s, 3 H, NCH_3), 2.76 (q, $^3J_{HH}$ 6.8, 2 H, CH_2CH_3), 2.87 (d, $^2J_{HH}$ 16.0, 2 H, CH_2CO_2), 3.11 (q, $^3J_{HH}$ 6.8, 2 H, CH_2CH_3), 3.28 (d, $^2J_{HH}$ 16.0, 2 H, CH_2 CO_2), 5.18 (d, $^3J_{HH}$ 18.0, 1 H, =C*H*B), 7.31 (m, 18 H, C_6H_5), 7.53 (m, 12 H, C_6H_5), 8.19 (d, $^3J_{HH}$ 18.0 Hz, 1 H, RuC*H*); $^{11}B\{^1H\}$: δ_B = 7.4; $^{13}C\{^1H\}(C_6D_6)$: δ_C = 12.00 (NCH_2CH_3), 12.61 (NCH_2CH_3), 43.63, 44.10, 44.43 (NCH_2 x 3) (NCH_3), 60.51 (NCH_2CH_3), 128.4 [$C^4(C_6H_5)$], 129.4 (CHB), 134.5 [t^v, J_{CP} 21.4, $C^1(C_6H_5)$], 135.2 [t^v, J_{CP} 5.7, $C^{3,5}(C_6H_5)$], 167.3 [OC(O)], 172.5 (RuCH), 205.7 (RuCO), 209.8 (CS_2), $C^{2,6}(C_6H_5)$ obscured by C_6D_6. $^{31}P\{^1H\}$: δ_P = 38.40. Acc. Mass: Found: *m/z* = 1007.1435. Calcd. for $C_{49}H_{49}{}^{11}BN_2NaO_5P_2{}^{102}RuS_2$ 1007.1592 $[M+Na]^+$. ESI-MS(+ve ion): *m/z* = 877.2 $[M+NCMe-S_2CNEt_2]^+$, 802.1 $[M-CH=CHBMIDA]^+$, 581.0 $[M+NCMe-CH=CHMIDA-\ PPh_3]^+$, 512.0 $[Ru(PPh_3)(S_2CNEt_2)]^+$. IR (C_6H_6): ν_{CO} 1761, 1915 cm^{-1}; IR (CH_2Cl_2): ν_{CO} 1759, 1912 cm^{-1}; IR (KBr Plate): ν_{CO} 1760, 1911 cm^{-1}. C*rystal data*: $C_{49}H_{49}BN_2O_5P_2RuS_2.C_3H_6O$, M_r = 1041.98, T = 150(2) K, monoclinic, space group $P2_1/n$, a = 12.8444(4), b = 25.1664(7), c = 47.1159(13) Å, β = 91.700(3)°, V = 15223.4(8) $Å^3$, Z = 12, D_{calcd} = 1.364 Mgm^{-3}, μ(Cu Kα) = 4.27 mm^{-1}, yellow plate, 0.02 × 0.05 × 0.09 mm, 43,623 measured reflections with $2\theta_{max}$ = 144.6°, 27,038 independent reflections, 26,923 absorption-corrected data used in F^2 refinement, 1,797 parameters, 0 restraints, R_1 = 0.084, wR_2 = 0.168 for 16,072 reflections with $I > 2\sigma(I)$, CCDC 1037271.

Decomposition product $[Ru(S_2CNEt_2)Cl(CO)(PPh_3)_2]$ (22): An anaerobic solution of **20** in $CH_2Cl_2/CHCl_3$ was observed to slowly decompose over approximately 6 days. Yellow X-ray quality diffraction crystals were obtained from vapour diffusion of chloroform/hexane or chloroform/MeOH and colourless X-ray diffraction quality crystals were also obtained from vapour diffusion of benzene/hexane. Yield: 0.008 g (0.01 mmol, 8%). IR (DCM): ν_{CO} 1947 cm^{-1}. NMR ($CDCl_3$, 25°C): ^1H: δ_H = 1.15 (t, $^3J_{HH}$ 7.0, 6 H, CH_3), 2.97 (q, $^3J_{HH}$ 7.0 Hz, 4 H, CH_2), 7.19-7.41 (m, 30 H, C_6H_5); $^{31}P\{^1H\}$: δ_P = 35.97 (s). Acc. Mass: Found: *m/z* = 843.1337. Calcd. for $C_{44}H_{43}N_2OP_2{}^{102}RuS_2$ 843.1336 $[M+NCMe-Cl]^+$. ESI-MS(+ve ion): *m/z* = 802.1 $[M-Cl]^+$. *Crystal data*: $C_{42}H_{40}ClNOP_2RuS_2.2(CHCl_3)$, M_r = 1076.14, T = 150(2) K, triclinic, space group P-1 (No.2), a = 9.90371(17), b = 15.5276(3), c = 18.2972(3) Å, α = 66.3796(16), β = 77.3401(15), γ = 88.4075(14)°, V = 2509.67(8) $Å^3$, Z = 2, D_{calcd} = 1.424 Mgm^{-3}, μ(Cu Kα) 7.60 mm^{-1}, yellow block, 0.14 × 0.23 × 0.28 mm, 30,901 measured reflections with $2\theta_{max}$ = 144.6°, 9,887 independent reflections, 9838 absorption-corrected data used in F^2 refinement, 550 parameters, 0 restraints, R_1 = 0.035, wR_2 = 0.082 for 9,682 reflections with $I > 2\sigma(I)$, CCDC 1037276. *Crystal data* (Figure 12): $C_{42}H_{40}ClNOP_2RuS_2.CH_3OH$, M_r = 869.43, T = 150(2) K, monoclinic, space group $C2/c$, a = 14.6330(4), b = 16.6388(3), c = 17.4758(4) Å, β = 102.586(2)°, V = 4,152.68(17) $Å^3$, Z = 4, D_{calcd} = 1.391 Mgm^{-3}, μ(Mo Kα) 0.66 mm^{-1}, yellow prism, 0.09 × 0.12 × 0.46 mm, 17,610 measured reflections with $2\theta_{max}$ = 59.6°, 5,107 independent reflections, 5,089 absorption-corrected data used in F^2 refinement, 259 parameters, 0 restraints, R_1 = 0.033, wR_2 = 0.078 for 4,464 reflections with $I > 2\sigma(I)$, CCDC 1037277. *Crystal data*: $C_{42}H_{40}ClNOP_2RuS_2.2.5(C_6H_6)$, M_r = 1032.67, T = 150(2) K, triclinic, space group P-1 (No.2), a = 9.9889(5), b = 14.4392(12), c = 17.9821(13) Å, α = 83.116(6), β = 76.954(5), γ = 85.934(5)°, V = 2505.9(3) $Å^3$, Z = 2, D_{calcd} = 1.369 Mgm^{-3}, μ(Cu Kα) 4.72 mm^{-1}, Colourless prism, 0.02 × 0.03 × 0.31 mm, 13864 measured reflections with $2\theta_{max}$ = 140.2°, 8969 independent reflections, 8,915 absorption-corrected data used in F^2 refinement, 586 parameters, 30 restraints, R_1 = 0.118, wR_2 = 0.278 for 6,797 reflections with $I > 2\sigma(I)$, CCDC 1037273, CCDC 1037275.

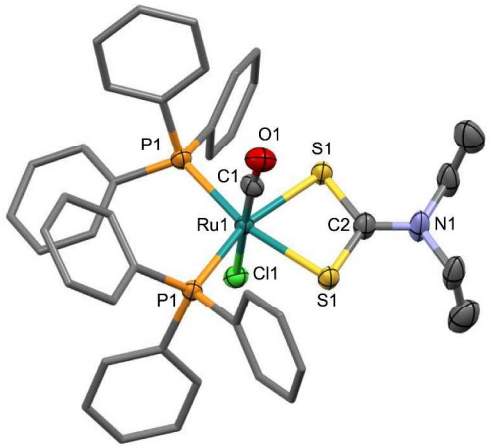


Fig. 12 Molecular structure of **22** in a crystal of **22**.MeOH**.** Depicted with 70% probability displacement ellipsoids. For clarity, hydrogen atoms have been omitted and phenyl groups simplified. Ru1, C1 and N1 lie on a crystallographic C_2 axis such that only half the molecule is unique. Selected bond distances [Å] and angles [°]: Cl1–Ru1 2.463(3), P1–Ru1 2.3782(6), Ru1–S1 2.4240(6), P1–Ru1–P1 108.15(3), S1–Ru1–S1 72.39(3).

The complex has been reported twice before[28,29] however both reports would now appear to be incorrect. It was claimed that this complex results from the reaction of $[Ru(NHSO_2C_6H_4{}^tBu\text{-}4)(CO)(S_2CNEt_2)(PPh_3)_2]$ with HCl,[28] however the reported ^1H NMR data (δ_H = 0.56, 0.75, 2.69, 3.01) are inconsistent with our own and with the crystal structure determinations and would suggest that the two ethyl groups to be chemically inequivalent. Specifically, the geometry adopted renders the ethyl groups chemically equivalent (as we observe) whilst the reported data indicate distinct ethyl environments. The second report claims that the complex results from the reaction of $[RuCl(NO)(CO)(PPh_3)_2]$ with $Na[Et_2NCS_2]$[29] however two phosphorus environments are reported (δ_P = 35.41, 27.07; $^2J_{PP}$ = 48 Hz) and the CO is claimed to give rise to a doublet resonance in the $^{13}C\{^1H\}$ NMR spectrum (δ_C = 201.65, $^2J_{PC}$ = 15 Hz). No ^1H NMR data were provided, however the $^{13}C\{^1H\}$ NMR data indicate a single ethyl environment. We therefore conclude that both reports are erroneous.

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Notes and references

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Table of Contents Text

The reactions of HC≡CBMIDA (BMIDA = $B(O_2CCH_2)_2NMe$) with a range of ruthenium complexes examples of σ-alkynyl, σ-alkenyl and vinylidene complexes bearing 4-coordinate boron substituents.