Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2015, **44**, 15470

# Diazoalkane complexes of ruthenium with tris(pyrazolyl)borate and bis(pyrazolyl)acetate ligands†

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Received 4th June 2015,
Accepted 16th July 2015

DOI: 10.1039/c5dt02113h

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Diazoalkane complexes [Ru(Tp)($N_2$CAr1Ar2)($PPh_3$)L]$BPh_4$ (**1** and **2**) [Tp = tris(pyrazolyl)borate; L = $P(OMe)_3$, $P(OEt)_3$; Ar1 = Ar2 = Ph; Ar1 = Ph, Ar2 = *p*-tolyl; Ar1Ar2 = $C_{12}H_8$] were prepared by allowing chloro-compounds RuCl(Tp)($PPh_3$)L to react with diazoalkane in the presence of $NaBPh_4$. Acrylonitrile $CH_2$=C(H)CN reacts with diazoalkane complexes to give 3*H*-pyrazole derivatives [Ru(Tp){N=NC(Ar1Ar2)CH(CN)$CH_2$}($PPh_3$){$P(OMe)_3$}]$BPh_4$ and [Ru(Tp){N=NC(Ar1Ar2)$CH_2$C(H)CN}($PPh_3$){$P(OMe)_3$}]$BPh_4$ (**3**). Diazoalkane complexes [Ru(bpza)($N_2$CAr1Ar2)($PPh_3$)$_2$]$BPh_4$ (**4**) [bpza = bis(pyrazolyl)acetate] were also prepared. All complexes were characterised by IR and NMR spectroscopy and X-ray crystal structure determination of [Ru(Tp){$N_2$C(Ph)(*p*-tolyl)}($PPh_3$){$P(OMe)_3$}]$BPh_4$ (**1b**). The differences exhibited by [Ru(Tp){$N_2$C(Ph)(*p*-tolyl)}($PPh_3$){$P(OMe)_3$}]$^+$ and [Ru(Cp){$N_2$C(Ph)(*p*-tolyl)}($PPh_3$){$P(OMe)_3$}]$^+$, as regards coordination of the diazoalkane ligand and reactivity towards alkenes, were explained on the basis of a comparative DFT study.

## Introduction

The chemistry of transition metal complexes containing diazoalkanes as ligands [M]–$N_2$CAr1Ar2 has long been under development[1–4] not only because of their potential use in the synthesis of carbene complexes[5,6] but mainly due to the different coordination modes and reactivities shown by the coordinate $N_2$CAr1Ar2 group.[1–4,7–10] In addition, diazoalkane complexes may be of interest as models for understanding $N_2$ coordination and functionalisation.[11,12]

A number of diazoalkane complexes of several metals have been reported[1–4,7–10] and their reactivity studies have highlighted various pathways, depending on the coordination mode and the nature of ancillary ligands. Thus, extrusion of dinitrogen with carbene formation was observed in $\eta^2$-CN-coordinated species,[4f,5,6] whereas an $\eta^1$-N-bound diazoalkane can yield dinitrogen [M]–$N_2$ complexes,[4f] convert carbene to imine,[5f] or cleave the N–N bond of the $N_2$CAr1Ar2 group.[4g] Dipolar (3 + 2) cycloaddition of coordinated diazoalkane with alkene and alkyne, affording 3*H*-pyrazole derivatives,[8] as well as hydrolysis, yielding $\eta^2$-diazene derivatives has recently been reported.[9]

In recent years, we have been interested in the chemistry of diazoalkane complexes[7–10,13] and have reported the synthesis and reactivity of these types of compounds having *p*-cymene, $\eta^5$-$C_5H_5$, $\eta^5$-$C_5Me_5$ and indenyl as supporting ligands. As the reactivity of the coordinated $N_2$CAr1Ar2 group in these complexes is strongly influenced by the nature of ancillary ligands, we thought of extending our study to the comparable tris(pyrazolyl)borate (Tp) ligand,[14] to test whether stable diazoalkane complexes could be prepared and to understand how their properties changed.

The results of these studies, leading to the synthesis and reactivity of the first diazoalkane complexes with tris(pyrazolyl)borate and bis(pyrazolyl)acetate ligands, are reported here.

## Results and discussion

### Preparation of diazoalkane complexes with the Tp ligand

Tris(pyrazolyl)borate complexes[15] RuCl(Tp)($PPh_3$)L [L = $P(OMe)_3$, $P(OEt)_3$] react with an excess of diazoalkane Ar1Ar2$CN_2$ in the presence of $NaBPh_4$ to give diazoalkane derivatives [Ru(Tp)($N_2$CAr1Ar2)($PPh_3$)L]$BPh_4$ (**1** and **2**), which were isolated and characterised (Scheme 1).

The reaction proceeds with substitution of chloride by diazoalkane, and is strongly favoured by the presence of $NaBPh_4$

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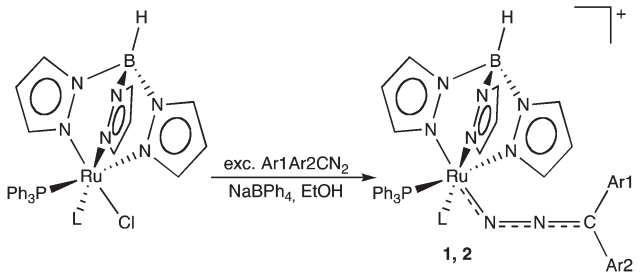
†Electronic supplementary information (ESI) available: DFT-optimised structures (.xyz file); Fig. S1, NMR spectra (pdf). CCDC 1404716. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt02113h




**Scheme 1** L = $P(OMe)_3$ (**1**), $P(OEt)_3$ (**2**); Ar1 = Ar2 = Ph (**a**); Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**).

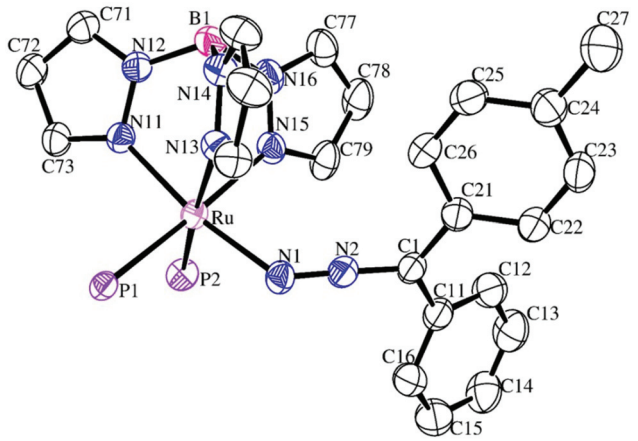


**Fig. 1** ORTEP view (30% probability level) of the cation **1b**. Hydrogen atoms, and phenyl rings at P1, and methoxy groups at P2 are omitted for clarity.

which, labilising the $Cl^-$ ligand, easily allows the formation of the final diazoalkane complexes **1** and **2**. Only mixed-ligand fragments $[Ru(Tp)(PPh_3)P(OR)_3]^+$ resulted in diazoalkane complexes, as bis(triphenylphosphine) species $RuCl(Tp)(PPh_3)_2$ turned out to be unreactive towards diazoalkane molecules.

The new diazoalkane complexes **1** and **2** were separated as yellow-orange solids stable in air and in solution of polar organic solvents, in which they behave as 1 : 1 electrolytes.[16] Analytical and spectroscopic (IR, NMR) data support the proposed formulation, which was further confirmed by X-ray crystal structure determination of $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**1b**), the ORTEP[17] of which is shown in Fig. 1.

The cation consists of a ruthenium atom coordinated by a Tp group, a $PPh_3$, a $P(OMe)_3$ ligand, and a *p*-tolyl(phenyl)-methylenediazo ligand. The asymmetric unit also contains a tetraphenylborate anion (not shown in Fig. 1). The ruthenium atom has a distorted octahedral arrangement of donor atoms. Selected bond distances and angles are listed in Table 1. The facial coordination of the Tp ligand is similar to those found, for example, in $RuTp(PPh_3)_2N_3$ [18] or in the cationic compounds $[RuTp(=C=CHR)(\kappa^2P,N\text{-}^iPr_2PNHPy)]^+$ (ref. 19) and $[RuTp(CH_3NHNH_2)\{P(OEt)_3\}(PPh_3)]^+$.[20] The $N_{Tp}$–Ru–$N_{Tp}$ angles are between 84.08(11) and 87.97(11)° and the Ru–$N_{Tp}$ bond distances are between 2.080(3) and 2.160(3) Å. Of these, the Ru–N(11) bond length is the shorter one and *trans* to this bond is the diazoalkane ligand, which exerts a *trans* influence lower than phosphines. The difference between the Ru–P bond lengths, 2.2458(9) and 2.3585(8) Å, is due to the different nature of the phosphane ligands.[8a,20] The *trans* angle [N(1)–Ru–N(11)] formed by the diazoalkane ligand, 170.17(11)°, together with the *cis* angle N(1)–Ru–N(13) of 84.80(11)°, shows a deviation of the diazoalkane ligand from the equatorial plane, although it is lower than that found in the methylhydrazine derivative.[20]

**Table 1** Selected bond lengths [Å] and angles [°] for **1b**

| | | | |
|---|---|---|---|
| Ru–N(1) | 2.038(3) | Ru–N(11) | 2.080(3) |
| Ru–N(15) | 2.142(3) | Ru–N(13) | 2.160(3) |
| Ru–P(2) | 2.2458(9) | Ru–P(1) | 2.3585(8) |
| N(1)–N(2) | 1.168(4) | N(2)–C(1) | 1.292(5) |
| C(1)–C(21) | 1.469(6) | C(1)–C(11) | 1.477(6) |
| | | | |
| N(1)–Ru–N(11) | 170.17(11) | N(1)–Ru–N(15) | 86.91(12) |
| N(1)–Ru–N(13) | 84.80(11) | N(11)–Ru–N(15) | 85.73(11) |
| N(11)–Ru–N(13) | 87.97(11) | N(15)–Ru–N(13) | 84.08(11) |
| N(1)–Ru–P(2) | 93.64(9) | N(11)–Ru–P(2) | 92.98(8) |
| N(15)–Ru–P(2) | 90.90(9) | N(13)–Ru–P(2) | 174.81(8) |
| N(1)–Ru–P(1) | 93.58(8) | N(11)–Ru–P(1) | 93.17(8) |
| N(15)–Ru–P(1) | 174.86(9) | N(13)–Ru–P(1) | 90.87(8) |
| P(2)–Ru–P(1) | 94.17(3) | N(2)–N(1)–Ru | 132.5(3) |
| N(1)–N(2)–C(1) | 178.2(4) | N(2)–C(1)–C(21) | 117.8(3) |
| N(2)–C(1)–C(11) | 116.9(4) | C(21)–C(1)–C(11) | 125.2(3) |

The most important feature in the compound is the bonding mode of the *p*-tolyl(phenyl)methylenediazo ligand.[1] The coordination of the diazoalkane ligand is clearly bent, with an N–N–Ru angle of 132.5(3)°, a more acute value than that found for this ligand in the cyclopentadienyl derivative $[RuCp\{NNC(Ph)Tol\}\{P(OEt)_3\}(PPh_3)]^+$, 156.0(5)°,[8a] or even in the diazofluorene derivatives $RuCl_2[NNC(C_{12}H_8)](PNP)$, 158.3(2)°,[21] and $[RuInd\{NNC(C_{12}H_8)\}(PPh_3)\{P(OEt)_3\}]^+$, 150.5(2)°.[10] However, the N–N–C angle is almost linear, 178.2(4)° *vs.* 173.9(6)° or 171.2(3)° for the above-mentioned RuCp and RuInd compounds. The N–N bond length, 1.168(4) Å, is slightly longer than in the mentioned compounds, 1.147(6) and 1.154(3) Å, and the N(2)–C(1) bond length, 1.292(5) Å is in practice the same length as that of the already mentioned Cp and Ind Ru compounds, 1.299(8) Å. However, the Ru–N bond length, 2.038(3) Å, is longer than those in the cited RuCp and RuInd compounds, 1.974(5) and 1.990(2) Å, respectively, or in other diazoalkane ruthenium complexes.[22] The short N–N bond distance may be viewed as between an N–N double and triple bond, and the N–C bond distance is short enough to be considered as a double bond. Angles around C(1) are close to 120° (from 116.9(4) to 125.2(3)°) and have a sum of 359.9°, thus confirming the $sp^2$ character of this atom, and consequently the nature of the diazoalkane ligand, besides the long Ru–N bond length and the acute Ru–N–N bond angle. Fig. 2 compares the structures of the cyclopentadienyl[8a] and tris(pyrazolyl)borate derivatives, and clearly shows the deviation of the Ru–N–N angle from linearity.

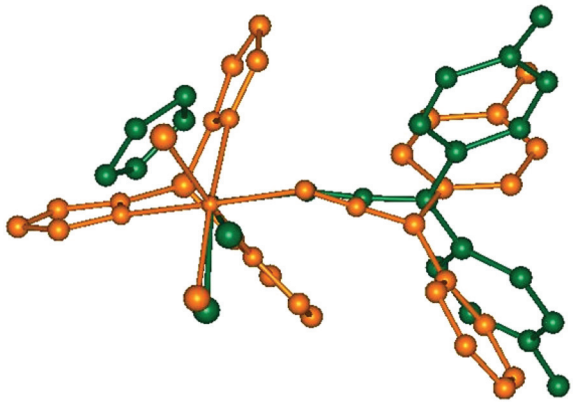


Fig. 2 Structural comparison between the Cp (green, ref. 8*a*) and Tp (orange, **1b**) derivatives.

Table 2 Selected experimental (X-ray) and computed (M06 and ωB97X functionals) bond lengths [Å] and angles [°] for the Ru-coordinated diazoalkane in the cation of **1b**

| | X-ray | M06 | ωB97X |
|---|---|---|---|
| Ru–N | 2.038(3) | 2.031 | 2.078 |
| N–N | 1.168(4) | 1.178 | 1.166 |
| N–C | 1.292(5) | 1.288 | 1.281 |
| Ru–N–N | 132.5(3) | 131.6 | 132.3 |
| N–N–C | 178.2(4) | 174.6 | 174.9 |

It is worth noting that single metal end-on or $\eta^1$-N-coordination of the diazoalkane ligand may be single-bent (with M–N–N angles close to 180°, N–N–C close to 120°, and $sp^2$ character at the nitrogen atom) or double-bent, when both angles are close to 120°. The coordination mode with a more acute M–N–N angle than the almost linear N–N–C is rarely found.[8a,21,22] The coordination mode or the diazoalkane ligand in **1b** may be ascribed to the steric factors and the crystal packing forces, as previously proposed for rhodium complexes with a Rh–N–N angle of 142.1(3)°.[23,24]

However, this hypothesis was ruled out when the geometry of the cation of **1b** was optimised at the DFT level (M06 and ωB97X functionals, gas-phase calculations). The computed internal coordinates match the experimental data well, as shown in Table 2 (see ESI† for the Cartesian coordinates of the DFT-optimised structures). For this reason, we analysed the occupied MOs in **1b** and in the analogous cyclopentadienyl derivative. The orbitals involved in the σ-type interactions inside the NNC moiety do not meaningfully overlap with the Ru-centred orbitals. Similar considerations may be made for the π-bonding NNC and NN orbitals of the diazoalkane ligand. The interaction between the metal centre and the diazoalkane is mainly attributable to the donation from the HOMO of the ligand, which has an N–C π-bonding character and π-antibonding for the N–N bond. As sketched for clarity in Fig. 3, the p-type orbital located on the coordinating nitrogen atom may overlap with ruthenium with either only one lobe or both. The former case is found in the HOMOs of both Tp and Cp complexes, and the latter in lower-energy occupied orbitals (HOMO−19 and HOMO−15 for Tp and Cp derivatives, respectively).

These high- and low-energy molecular orbitals, shown in Fig. 3, evidently have opposite effects on the coordination mode of the diazoalkane. An increase in the metal–ligand overlap in the HOMOs causes a decrease in the Ru–N–N angle, whereas the interaction occurring in the lower-energy MOs flattens the angle. Analysis of the HOMO of $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ showed that diazoalkane orbitals contribute 75% in the building of this MO, while the contribution of the metal centre is 16%. In contrast, the metal centre is less involved in the HOMO of $[Ru(Cp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ (diazoalkane: 85%; ruthenium: 8%). The opposite occurs when lower-energy orbitals are compared: in the HOMO−19 of the Tp complex, the contribution of the diazoalkane is much greater (61%) than that of ruthenium (13%), whereas the values are more comparable (diazoalkane: 34%; ruthenium: 15%) in the Cp derivative. The contribution of the Cp ligand for building of HOMO−15 is higher than that of the Tp to HOMO−19, and supports metal–diazoalkane interaction. As a result, the change in the Ru–N–N angle when the ancillary ligand is varied reflects different Ru–diazoalkane overlaps in the occupied MOs, which are influenced by the other species in the coordination sphere.

The IR spectra of diazoalkane complexes **1** and **2** show a weak band at 2488–2481 $cm^{-1}$, attributed to the $\nu_{BH}$ of the Tp ligand and a medium-intensity resonance at 1980–1936 $cm^{-1}$, attributed to the $\nu_{C=N=N}$ of the coordinated diazoalkane. Comparison of these values with literature data[1–4,7–10] also suggests the end-on $\eta^1$-coordination mode of the $Ar1Ar2CN_2$ group, similar to that found in the solid state for **1b**. Besides the signals of the ancillary ligands Tp, $PPh_3$, $P(OR)_3$ and the $BPh_4^-$ anion, the $^1H$ NMR spectra of **1** and **2** show the signals characteristic of the substituents Ar1 and Ar2 of the diazoalkane, whereas the $^{31}P$ NMR spectra are AB systems, simulable with the parameters given in the Experimental section. The $^{13}C$ NMR spectra show the pyrazole carbon atom resonances between 148 and 106 ppm and the Cα signal of the $N_2CAr1Ar2$ at 84–83 ppm, fitting the proposed formulation for the complexes.

### Reactions with alkenes and alkynes

The reactions of diazoalkane complexes **1** and **2** with several alkenes were extensively studied, and the results are summarised in Scheme 2.

Under mild conditions (1 atm, RT), ethylene $CH_2{=}CH_2$ does not react with diazoalkane complexes **1** and **2** and the starting materials could be recovered unchanged after 24 h of reaction.

This result was rather surprising because the comparable Cp complexes $[Ru(\eta^5\text{-}C_5H_5)(N_2CAr1Ar2)(PPh_3)\{P(OEt)_3\}]BPh_4$ did react with ethylene to give, besides substitution of the $Ar1Ar2CN_2$ ligand, (3 + 2) cycloaddition, affording 3*H*-pyrazole

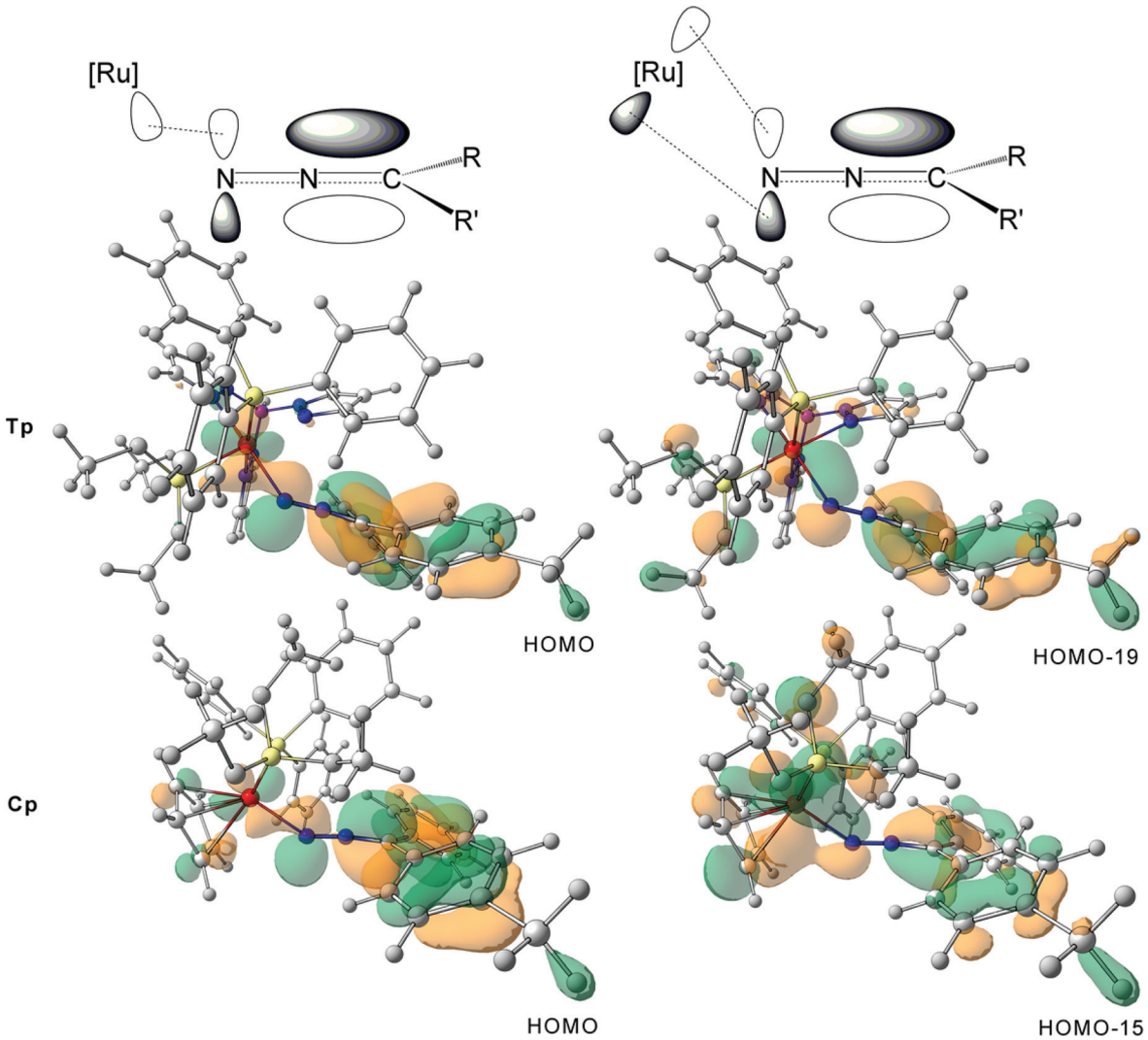
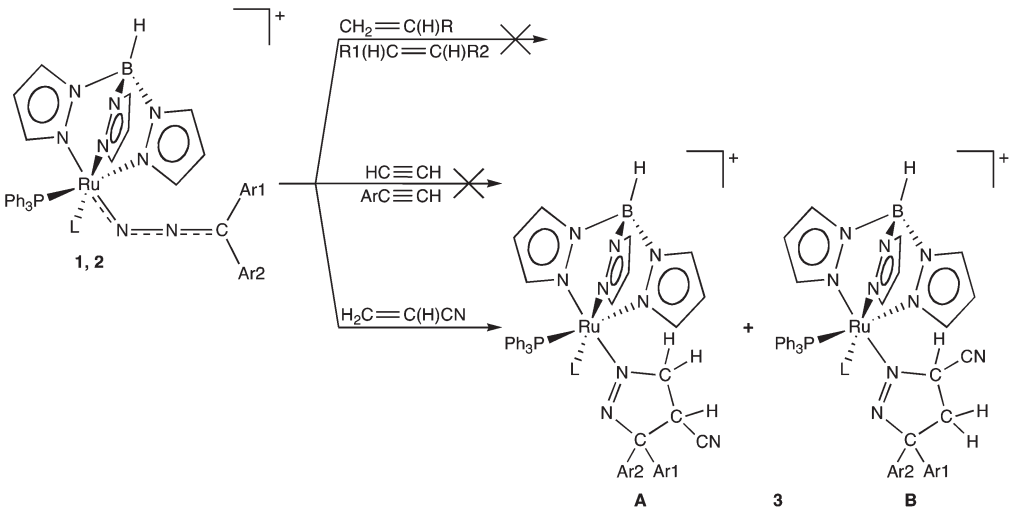



**Fig. 3** Sketches of the interactions between the metal centre and the diazoalkane ligand and selected occupied MOs (ωB97X DFT functional, surface isovalue = 0.03 a.u.) for $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ and $[Ru(Cp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$. Color map: grey, hydrogen and carbon; blue, nitrogen; red, ruthenium; yellow, phosphorus; violet, boron.

derivatives.[8] In our Tp complexes neither substitution nor cycloaddition occurred, so the coordinated diazoalkane were unreactive towards $CH_2{=}CH_2$.

As reported in the literature,[25] the cyclisation reactions are attributable to the overlap between the HOMO of diazoalkane and the LUMO of ethylene. Computations show that the $HOMO_{diazomethane}/LUMO_{ethene}$ interaction stabilises the transition state of the 1,3-dipolar cycloaddition to ethene by about 11 kcal $mol^{-1}$. Computations also show that the $HOMO_{ethene}/LUMO_{diazomethane}$ interaction contributes to further stabilisation of 7 kcal $mol^{-1}$.[25] As described before, in our case, the HOMO of coordinated diazoalkane was part of the occupied frontier orbital in both $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ and $[Ru(Cp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$. The HOMO energy values of the complexes are closely comparable and do not explain the different reactivities (−9.945 and −9.919 eV for the Tp and Cp derivatives, respectively; ωB97X functional). As regards the empty MOs, the LUMO of $[Ru(Cp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ ($\varepsilon$ = −1.815 eV) shows the correct symmetry to interact with the HOMO of ethylene, and the lobes on the NNC moiety are roughly perpendicular to the plane defined by the three σ-bonds of the carbon atom (see Fig. 4). Instead, the LUMO of the Tp derivative is not suitable for interactions with ethylene, because the lobes are parallel to the previously defined plane and the interaction with ethylene is prevented by the bulk of the aryl substituents. The LUMO+1 is the empty MO of $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$, more similar to the LUMO of the Cp complex, but its energy is significantly higher, −1.223 eV. As shown in Fig. 4, the lower energy of the LUMO in the Cp derivative appears to be attributable to higher contribution of the metal centre to the combination. We therefore propose that the lack




**Scheme 2** L = $P(OMe)_3$; R = H, $CH_3$, Ph; R1R2 = C(O)OCO (maleic anhydride); R1 = R2 = COOMe.

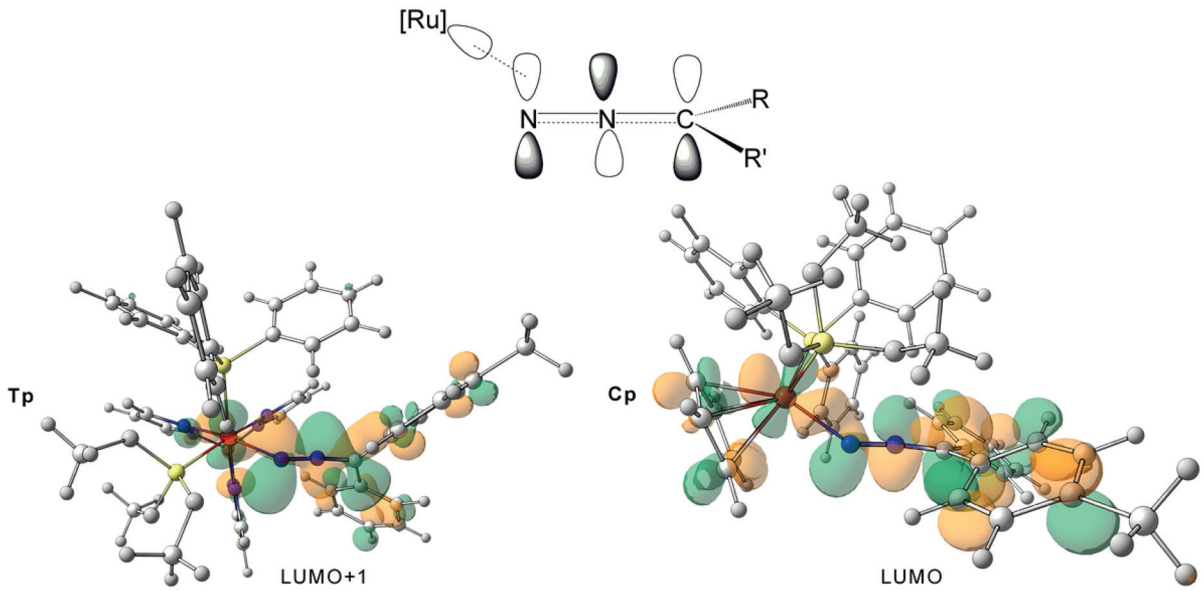



**Fig. 4** Sketch and pictures for selected unoccupied MOs (ωB97X DFT functional, surface isovalue = 0.03 a.u.) of $[Ru(Tp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$ and $[Ru(Cp)\{N_2C(Ph)(p\text{-tolyl})\}(PPh_3)\{P(OMe)_3\}]^+$. Color map: grey, hydrogen and carbon; blue, nitrogen; red, ruthenium; yellow, phosphorus; violet, boron.

of reactivity towards cycloadditions of diazoalkane complexes having Tp in the coordination sphere may be ascribed to the excessively high energy of the unoccupied orbital involved in such reactions.

We extended our reactivity study to other alkenes and observed that propylene and styrene also do not react with diazoalkane complexes **1** and **2**. Instead, acrylonitrile quickly reacts with **1** to give the 3*H*-pyrazole complexes $[Ru(Tp)\{\overline{N{=}NC(Ar1Ar2)CH(CN)CH_2}\}(PPh_3)\{P(OMe)_3\}]BPh_4$ and $[Ru(Tp)\{\overline{N{=}NC(Ar1Ar2)CH_2C(H)CN}\}(PPh_3)\{P(OMe)_3\}]BPh_4$ (**3**), which were isolated as a mixture of the **A** and **B** isomers (ratio about 1 : 1) and characterised. The reaction proceeds with (3 + 2) cycloaddition of $CH_2{=}C(H)CN$ to the coordinated diazoalkane, affording 3,5-dihydro-3*H*-pyrazole derivatives **3**, and seems to be favoured by the presence of an electron-withdrawing group such as C≡N. Surprisingly, the reaction of other activated alkenes such as maleic anhydride [$\overline{CH{=}CHCO(O)CO}$, ma] and dimethylmaleate [$CH_3OCOC(H){=}C(H)COOCH_3$, dmm] does not proceed, and neither cyclisation nor substitution of the $Ar1Ar2CN_2$ ligand occurs, leaving the starting complexes unchanged after 24 h of reaction. Therefore, it seems that only activated alkenes with low steric hindrance such as $CH_2{=}C(H)$-CN react with diazoalkanes coordinate to $[Ru(Tp)(PPh_3)L]^+$ fragments, whereas alkenes with either electron-donor groups

($CH_2$═C(H)$CH_3$, $CH_2$═C(H)Ph) or bulkier substituents (ma, dmm) do not. These results also show that the Ar1Ar2$CN_2$ ligand is very stable towards substitution in our Tp derivative as compared with the cyclopentadienyl homologous,[8] which easily undergoes substitution with either $CH_2$═$CH_2$ or ma and dmm, affording the $\eta^2$-alkene derivative.

Acetylene and terminal alkynes were also tested in the reaction with diazoalkane complexes **1** and **2** but, in this case too, no reaction was observed at room temperature and only decomposition occurred at reflux.

Comparison between complexes **1** and **2** and related diazoalkane complexes with the cyclopentadienyl ligand, [Ru(Cp)($N_2$CAr1Ar2)($PPh_3$)L]$BPh_4$,[8] showed that both fragments can bond with the diazoalkane group, whereas the Cp fragment activates Ar1Ar2$CN_2$ for easy (3 + 2) cycloaddition with alkenes and alkynes, together with substitution reactions, the Tp fragment makes Ar1Ar2$CN_2$ rather unreactive towards cycloaddition and substitution reactions, as only highly-activated dipolarophiles such as acrylonitrile can react with the coordinated diazoalkane to yield 3*H*-pyrazole derivatives **3**.

In addition, it is worth noting that the reaction with $CH_2$═C(H)CN of the related diazoalkane complexes[8,10] [Ru($\eta^5$-$C_5H_5$)($N_2$CAr1Ar2)($PPh_3$)L]$BPh_4$ and [Ru($\eta^5$-$C_9H_7$)($N_2$CAr1Ar2)($PPh_3$)L]$BPh_4$ (L = phosphites) affords the 1*H*-pyrazoline derivatives [Ru]-$\eta^1$-N═C(CN)$CH_2$C(Ar1Ar2)NH, probably through tautomerisation of the first cyclisation product, the 3*H*-pyrazole species [Ru]-$\eta^1$-N═NC(Ar1Ar2)$CH_2$C(H)CN. Instead, the Tp ligand stabilises the 3*H*-pyrazole molecule formed through (3 + 2) cycloaddition, allowing the separation of **3** as a stable solid and highlights that both cyclisation modes of the nitrile occur in Tp complexes, affording both isomers **A** and **B** in comparable yields.

Complexes **3** were isolated as reddish-orange solids stable in air and in solution of polar organic solvents, in which they behave as 1 : 1 electrolytes.[16] Analytical and spectroscopic (IR and NMR) data support their proposed formulation. The IR spectra show a weak band at 2487–2482 $cm^{-1}$ due to the $\nu_{BH}$ of the Tp ligand and another weak absorption at 2240–2235 $cm^{-1}$ attributed to the $\nu_{CN}$ of the 3*H*-pyrazole ligand. The $^1$H and $^{31}$P NMR spectra of complex **3c**, containing the fluorenyl substituent at the C3 carbon atom of pyrazole, show several sets of signals for both 3*H*-pyrazole protons (see ESI, Fig. S1†) and $^{31}$P nuclei of phosphines, suggesting the presence of more isomers that we were not able to separate. Cyclisation reaction with $CH_2$═C(H)CN afforded two different 3*H*-pyrazole ligands, depending on the cyclisation mode of the nitrile, thus allowing the formation of the two complexes: [Ru(Tp)-{N═NC(Ar1Ar2)CH(CN)$CH_2$}($PPh_3$){$P(OMe)_3$}]$BPh_4$ (**A**) and [Ru(Tp){N═NC(Ar1Ar2)$CH_2$C(H)CN}($PPh_3$){$P(OMe)_3$}]$BPh_4$ (**B**), shown in Scheme 2. In addition, the presence of two stereocentres in the molecule, *i.e.*, ruthenium and the C(CN) atom of the heterocyclic ligand, gave a mixture of two diastereoisomers, which were obtained in about 1 : 1 ratio. In the 3*H*-pyrazole region (1–3 ppm), the proton NMR spectrum of complex **3c** showed three multiplets, simulable with an ABC model (Fig. S1†) with the parameters reported in the Experimental section and attributed to the H4 and H5 protons of the pyrazole ligand (Chart 1).

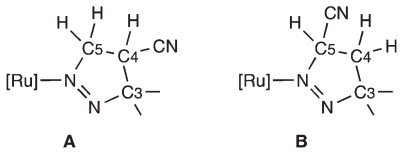



Chart 1

Two of these multiplets were attributed to the two diastereoisomers of complex **A**, and the third to those of **B**. In this case, the two multiplets probably overlapped within the linewidth of the spectra. The $^{31}$P{$^1$H} NMR spectrum of **3c** shows four AB systems, due to the presence of the two isomeric species **A** and **B** and of two diastereoisomers for each of them. In fact, in the temperature range from +20 to −80 °C, only two AB systems were observed, attributable to the two diastereoisomers by comparison with related systems.[8a] Instead, the influence of the 3*H*-pyrazole ligand on the $^{31}$P parameters of isomers **A** and **B** is probably so small that the spectra overlapped.

Besides the signals of the ancillary ligands Tp, $PPh_3$ and $P(OMe)_3$ and the $BPh_4$ anion, the $^{13}$C NMR spectrum of **3c** shows the resonances of the C3, C4 and C5 pyrazole carbon atoms near 36, 21 and 15 ppm, respectively, fitting the proposed formulation for the complexes. It is noteworthy that the reaction with acrylonitrile of the related cyclopentadienyl complex [Ru($\eta^5$-$C_5H_5$){$N_2$C(Ph)(*p*-tolyl)}($PPh_3$){$P(OMe)_3$}]$BPh_4$ affords, as the final product, the 1*H*-pyrazoline derivative [Ru($\eta^5$-$C_5H_5$){$\eta^1$-N═C(CN)$CH_2$C(Ph)(*p*-tolyl)NH}($PPh_3$){$P(OMe)_3$}]-$BPh_4$ formed by tautomerisation of the first cyclisation product, 3*H*-pyrazole. In our case, the NMR data indicate that no tautomerisation occurs, so 3*H*-pyrazole complex **3c** was the only species isolated.

The $^1$H NMR spectrum of complexes [Ru(Tp)-{N═NC(Ph)(*p*-tolyl)CH(CN)$CH_2$}($PPh_3$){$P(OMe)_3$}]$BPh_4$ and [Ru(Tp){N═NC(Ph)(*p*-tolyl)$CH_2$C(H)CN}($PPh_3$){$P(OMe)_3$}]$BPh_4$ (**3b**), containing three diastereocentres in the molecule, showed a very complicated set of multiplets between 3.55 and 1.18 ppm, attributable to the H4 and H5 protons of the 3*H*-pyrazole ligands and several doublets of the $P(OMe)_3$ hydrogens at 3.19–3.07 ppm, suggesting the presence of several isomers and diastereoisomers. However, the multiplets partly overlapped and parameters could not be unambiguously attributed. The $^{31}$P NMR spectrum of **3b** also showed several AB systems, whereas the $^{13}$C spectrum revealed some sets of signals characteristic of the C3, C4 and C5 carbon atoms of the 3*H*-pyrazole ligand, near 40, 22 and 13 ppm, respectively, matching the proposed formulation for the complexes.

### Complexes with other scorpionates

The results obtained with the Tp ligand prompted us to extend our study to other pyrazolyl ligands, such as bis(pyrazol-1-yl)-

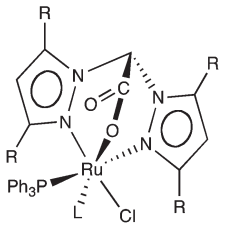
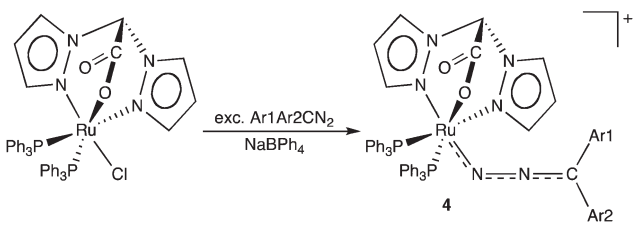


Chart 2 L = $PPh_3$, $P(OMe)_3$; R = H (bpza), $CH_3$ (bdmpza).



Scheme 3 Ar1 = Ph, Ar2 = *p*-tolyl (**b**); Ar1Ar2 = $C_{12}H_8$ (**c**).

acetate (bpza) and the related bis(methyl) (bdmpza), the ruthenium complexes of which are shown in Chart 2.

We prepared the bis(triphenylphosphine) complexes,[26] $RuCl(bpza)(PPh_3)_2$ and $RuCl(bdmpza)(PPh_3)_2$, and the mixed-ligand phosphine–phosphite ones, $RuCl(bpza)(PPh_3)[P(OMe)_3]$ and $RuCl(bdmpza)(PPh_3)[P(OMe)_3]$, and studied their reactivity towards diazoalkane molecules. The results show that only the triphenylphosphine complex, $RuCl(bpza)(PPh_3)_2$, reacts with $Ar1Ar2CN_2$, in the presence of $NaBPh_4$, to give diazoalkane complexes, $[Ru(bpza)(N_2CAr1Ar2)(PPh_3)_2]BPh_4$ (**4**), which were isolated and characterised (Scheme 3). The reaction proceeds with the substitution of the chloride ligand by $Ar1Ar2CN_2$ and is favoured by the presence of $NaBPh_4$ which, labilising $Cl^-$, allows the formation of **4** in good yield.

Instead, the bis(dimethylpyrazolyl)acetate (bdmpza) complex $RuCl(bdmpza)(PPh_3)_2$ and the mixed-ligand ones, $RuCl(bpza)(PPh_3)[P(OMe)_3]$ and $RuCl(bdmpza)(PPh_3)[P(OMe)_3]$, did not yield any diazoalkane complexes. At room temperature, the starting complexes were unreactive towards $Ar1Ar2CN_2$, but decomposition occurred under reflux, preventing the formation of pure products.

Bis(pyrazolyl)acetate therefore confers different properties on the ruthenium fragment with respect to tris(pyrazolyl)borate, showing the ability to stabilise a diazoalkane complex in only one case, with two $PPh_3$ ligands.

Complexes $[Ru(bpza)(N_2CAr1Ar2)(PPh_3)_2]BPh_4$ (**4**) were isolated as green solids stable in air and in solution of polar organic solvents, in which they behave as 1 : 1 electrolytes.[16] Analytical and spectroscopic data support the proposed formulation for the complexes. In particular, the IR spectra show a medium-intensity band at 1959–1900 $cm^{-1}$, attributed to the $\nu_{C=N=N}$ of the coordinated diazoalkane. Comparison of this value with those of the related complexes whose X-ray structures are known[1–4,7–10] suggests an end-on $\eta^1$-coordination mode for the $Ar1Ar2CN_2$ ligand. In the spectra, a strong band at 1672–1669 $cm^{-1}$ is also present, and was attributed to the $\nu_{CO}$ of the carboxylate group of the bpza ligand. The $^1H$ NMR spectra show the signals characteristic of the pyrazole hydrogen atoms of bpza between 7.42 and 5.81 ppm and those of the substituents Ar1Ar2 of the diazoalkane ligand, whereas the $^{31}P$ NMR spectra are singlets at 35.60–34.29 ppm. Besides the signals of $PPh_3$ and the $BPh_4$ anion, the $^{13}C$ NMR spectra of **4b** show a singlet at 163.99 ppm of the carboxylate $COO^-$ and another one at 75.10 ppm of the methine C(H)COO carbon resonance of the bpza ligand. Singlets at 134.93, 146.07 and 109.11 ppm were attributed to the C3, C5 and C4 resonances, respectively, of the pyrazole group of bpza, and the singlet at 88.44 ppm was assigned to the diazoalkane $CN_2$ carbon resonance, matching the proposed formulation.

Some reactivity studies on diazoalkane complexes **4** were performed with alkenes and alkynes, to test whether substitution or (3 + 2) cycloaddition occurred. Unfortunately, no results were obtained, as the starting $Ar1Ar2CN_2$ complexes **4** were unreactive under mild conditions (RT, 1 atm, 4 to 10 h of reaction), although unidentified decomposition products were obtained under reflux conditions.

## Conclusions

In this paper we demonstrate that stable diazoalkane complexes of ruthenium can be prepared with both tris(pyrazolyl)borate (Tp) and bis(pyrazolyl)acetate (bpza) as supporting ligands. Reactivity studies indicated that $Ar1Ar2CN_2$ complexes are robust towards substitution and cyclisation reactions with alkene and alkyne, and only with $CH_2{=}C(H)CN$ does (3 + 2) cycloaddition occur, affording 3*H*-pyrazole derivatives. The results of a DFT study on both coordination of diazoalkanes and their reactivity is also reported.

## Experimental

### Materials and physical measurements

All synthetic work was carried out under an appropriate atmosphere (Ar, $N_2$) using standard Schlenk techniques or in an inert atmosphere dry-box. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3{\cdot}3H_2O$ was a Pressure Chemical Co. (USA) product; phosphites $P(OMe)_3$ and $P(OEt)_3$ were Aldrich products used as received; diazoalkanes were prepared following a known method;[27] other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra ($^1H$, $^{13}C$, and $^{31}P$) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between −90 and +25 °C, unless otherwise mentioned. $^1H$ and $^{13}C$ spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are

reported with respect to 85% $H_3PO_4$, with downfield shifts considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package[28] was used to treat NMR data. The conductivity of $10^{-3}$ mol dm$^{-3}$ solutions of the complexes in $CH_3NO_2$ at 25 °C was measured using a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

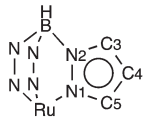
### Synthesis of the complexes

Precursor complexes RuCl(Tp)$(PPh_3)_2$ and RuCl(Tp)$(PPh_3)$L [Tp = tris(pyrazolyl)borate; L = $P(OMe)_3$, $P(OEt)_3$], RuCl(bpza)$(PPh_3)_2$ and RuCl(bdmpza)$(PPh_3)_2$ [bpza = bis(pyrazol-1-yl)acetate; bdmpza = bis(3,5-dimethylpyrazol-1-yl)acetate] were prepared following the methods previously reported.[15,26,29]

**RuCl(bpza)$(PPh_3)$[$P(OMe)_3$].** A slight excess of trimethylphosphite (0.52 mmol, 62 μL) was added to a solution of RuCl(bpza)$(PPh_3)_2$ (0.40 g, 0.44 mmol) in benzene (25 mL) and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with diethylether (5 mL). The yellow-green solid which slowly formed was filtered and crystallised from dichloromethane and diethylether; yield ≥80%. IR (KBr, cm$^{-1}$) $\nu_{CO}$ 1650 (s); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 8.22–7.01 (m, 17H, Ph + H3 bpza), 6.88 (s, 1H, CH bridging bpza), 6.42 (br, 2H, H5 bpza), 5.99 (t, $J_{HH}$ = 2.5, 2H, H4 bpza), 3.36 (d, 9H, $CH_3$); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 143.39, $\delta_B$ 51.71, $J_{AB}$ = 63.6 Hz; Anal. Calcd for $C_{29}H_{31}ClN_4O_5P_2Ru$ (714.05): C, 48.78; H, 4.38; Cl, 4.97; N, 7.85; Found: C, 48.66; H, 4.51; Cl, 5.05; N, 7.69%.

**RuCl(bdmpza)$(PPh_3)$[$P(OMe)_3$].** This complex was prepared exactly like the related bpza one but with a reaction time of 2 h; yield ≥85%. IR (KBr, cm$^{-1}$) $\nu_{CO}$ 1661 (s); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 7.50–6.97 (m, 15H, Ph), 6.47 (s, 1H, CH bridging bdmpza), 5.73 (s, 2H, H4 bdmpza), 3.15 (d, 9H, $CH_3$ phos), 2.45, 1.75 (s, 12H, $CH_3$ bdmpza); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 144.13, $\delta_B$ 47.05, $J_{AB}$ = 67.2 Hz; Anal. Calcd for $C_{33}H_{39}ClN_4O_5P_2Ru$ (770.16): C, 51.46; H, 5.10; Cl, 4.60; N, 7.27; Found: C, 51.61; H, 5.19; Cl, 4.42; N, 7.15%.

**[Ru(Tp)$(N_2CAr1Ar2)(PPh_3)$L]$BPh_4$ (1 and 2) [L = $P(OMe)_3$ (1), $P(OEt)_3$ (2); Ar1 = Ar2 = Ph (a); Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = $C_{12}H_8$ (c)].** In a 25 mL three-necked round-bottom flask were placed solid samples of RuCl(Tp)$(PPh_3)$L (0.2 mmol), an excess of $NaBPh_4$ (0.4 mmol, 137 mg), an excess of the appropriate diazoalkane (0.6 mmol) and 5 mL of ethanol. The reaction mixture was stirred for 24 h and the yellow solid that formed was filtered and crystallised from $CH_2Cl_2$ and EtOH. A further amount of solid was obtained by cooling the mother liquor to −25 °C; total yield ≥75%.




**1a**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2482 (w), $\nu_{N_2}$ 1942 (m); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 7.96–6.87 (m, 45H, Ph), 7.98 (d, $J_{HH}$ = 2.35), 7.93 (br), 7.76 (d, $J_{HH}$ = 1.6) (3H, H3 or H5 Tp), 7.53, 7.34 (d, $J_{HH}$ = 2.3), 6.62 (br) (3H, H5 or H3 Tp), 6.20 (t), 6.03 (br), 5.98 (t, $J_{HH}$ = 1.7) (3H, H4 Tp), 3.12 (d, 9H, $CH_3$); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 132.72, $\delta_B$ 41.77, $J_{AB}$ = 52.20; $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: 165–122 (m, Ph), 147.86 (br), 146.97 (d, $J_{CP}$ = 3.6), 144.31 (br) (C5 or C3 Tp), 138.55 (d, $J_{CP}$ = 2.6), 136.99 (d, $J_{CP}$ = 3.2), 136.62 (s br) (C3 or C5 Tp), 107.34 (d, $J_{CP}$ = 1.1), 107.13 (d, $J_{CP}$ = 3.8), 107.00 (t, $J_{CP}$ = 2.0) (C4 Tp), 83.50 (br, $CN_2$), 53.39 (d, $CH_3$, $J_{CP}$ = 11.2 Hz); Anal. Calcd for $C_{67}H_{64}B_2N_8O_3P_2Ru$ (1213.92): C, 66.29; H, 5.31; N, 9.23; Found: C, 66.10; H, 5.43; N, 9.09%; $\Lambda_M$ = 54.4 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

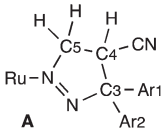
**1b**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2482 (w), $\nu_{N_2}$ 1939 (m); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 7.44–6.65 (m, 44H, Ph), 7.98 (d, $J_{HH}$ = 2.4), 7.94 (d, $J_{HH}$ = 1.9), 7.76 (d, $J_{HH}$ = 2.2) (3H, H3 Tp), 7.54 (d, $J_{HH}$ = 2.0), 7.35, 6.64 (br) (3H, H5 Tp), 6.20 (t, $J_{HH}$ = 2.3), 6.04 (dt, $J_{HH}$ = 2.2, $J_{PH}$ = 0.6) (3H, H4 Tp), 3.13 (d, 9H, $CH_3$ phos, $J_{PH}$ = 10.6), 2.39 (s, 3H, $CH_3$ *p*-tolyl); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 133.00, $\delta_B$ 42.00, $J_{AB}$ = 53.46; $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: 165–122 (m, Ph), 147.84 (s), 144.31 (d, $J_{CP}$ = 1.5), 143.94 (d, $J_{CP}$ = 4.6) (C5 Tp), 138.48 (br), 136.94 (d, $J_{CP}$ = 3.2), 136.56 (br) (C3 Tp), 107.28 (d, $J_{CP}$ = 0.4), 107.10 (d, $J_{CP}$ = 4.0), 106.91 (t, $J_{CP}$ = 2.2) (C4 Tp), 84.07 (br, $CN_2$), 53.33 (d, $CH_3$ phos, $J_{CP}$ = 9.2 Hz), 21.33 (s, $CH_3$ *p*-tolyl); Anal. Calcd for $C_{68}H_{66}B_2N_8O_3P_2Ru$ (1227.94): C, 66.51; H, 5.42; N, 9.13; Found: C, 66.37; H, 5.34; N, 9.26%; $\Lambda_M$ = 53.7 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

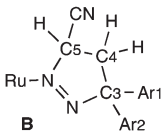
**1c**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2488 (w), $\nu_{N_2}$ 1980 (m); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 8.10–6.84 (m, 48H, Ph + H3 and H5 Tp), 6.24, 6.05 (m, 3H, H4 Tp), 3.21 (t, 9H, $CH_3$); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 129.54, $\delta_B$ 38.53, $J_{AB}$ = 52.25 Hz; Anal. Calcd for $C_{67}H_{62}B_2N_8O_3P_2Ru$ (1211.90): C, 66.40; H, 5.16; N, 9.25; Found: C, 66.52; H, 5.08; N, 9.11%; $\Lambda_M$ = 54.1 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**2b**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2481 (w), $\nu_{N_2}$ 1936 (m); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 7.40–6.62 (m, 44H, Ph), 7.91 (d, $J_{HH}$ = 2.3), 7.89 (d, $J_{HH}$ = 1.0), 7.75 (br) (3H, H3 or H5 Tp), 7.39, 7.37, 6.49 (br, 3H, H3 or H5 Tp), 6.10 (t, $J_{HH}$ = 2.2), 6.04 (t, $J_{HH}$ = 2.0), 5.92 (t, $J_{HH}$ = 1.7) (3H, H4 Tp), 3.57, 3.29 (m, 6H, $CH_2$), 2.37 (s, 3H, $CH_3$ *p*-tolyl), 0.99 (t, $J_{HH}$ = 7.0, 9H, $CH_3$ phos); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 128.93, $\delta_B$ 42.59, $J_{AB}$ = 52.25; $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: 165–122 (m, Ph), 143.97 (d, $J_{CP}$ = 3.0), 144.58, 144.29 (s) (C3 or C5 Tp), 138.2 (s), 136.9, 136.5, (br) (C3 or C5 Tp), 106.89 (br), 106.83, 106.73 (t br) (C4 Tp), 83.75 (s, $CN_2$), 62.73 (d, $CH_2$, $J_{CP}$ = 9.4), 21.29 (s, $CH_3$ *p*-tolyl), 15.98 (d, $CH_3$ phos, $J_{CP}$ = 6.5 Hz); Anal. Calcd for $C_{71}H_{72}B_2N_8O_3P_2Ru$ (1270.02): C, 67.15; H, 5.71; N, 8.82; Found: C, 66.94; H, 5.80; N, 8.73%; $\Lambda_M$ = 52.8 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**2c**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2488 (w), $\nu_{N_2}$ 1975 (m); $^1$H NMR ($CD_2Cl_2$, 20 °C) $\delta$: 8.00–6.70 (m, 49H, Ph + H3 and H5 Tp), 6.25 (t, br), 6.18 (t, $J_{HH}$ = 3.0), 6.02 (m) (3H, H4 Tp), 3.64, 3.37 (m, 6H, $CH_2$), 1.04 (t, 9H, $CH_3$); $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 125.37, $\delta_B$ 39.45, $J_{AB}$ = 52.25 Hz; Anal. Calcd for $C_{70}H_{68}B_2N_8O_3P_2Ru$ (1253.98): C, 67.05; H, 5.47; N, 8.94; Found: C, 66.87; H, 5.39; N, 9.06%; $\Lambda_M$ = 53.6 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**[Ru(Tp){N=NC(Ar1Ar2)CH(CN)CH$_2$}(PPh$_3$){P(OMe)$_3$}]BPh$_4$ (A) and [Ru(Tp){N=NC(Ar1Ar2)CH$_2$C(H)CN}(PPh$_3$){P(OMe)$_3$}]-BPh$_4$ (B) (3) [Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = C$_{12}$H$_8$ (c)].** An excess of acrylonitrile CH$_2$=C(H)CN (0.4 mmol, 26 μL) was added to a solution of the appropriate diazoalkane complex [RuTp(N$_2$CAr1Ar2)(PPh$_3$){P(OMe)$_3$}]BPh$_4$ (**1**) (0.13 mmol) in 10 mL of dichloromethane and the reaction mixture was stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL). A yellow solid slowly separated out, which was filtered and crystallised from CH$_2$Cl$_2$ and EtOH; yield ≥55%.

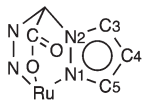



**3b**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2487 (w), $\nu_{CN}$ 2240 (w); $^1$H NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 7.98–5.40 (m, 53H, Ph + Tp), 3.55–1.18 (m, 3H, CH$_2$CH pz), 3.19, 3.17, 3.16, 3.09, 3.07 (d, 9H, CH$_3$ phos), 2.35, 2.30, 2.28, 2.18, 2.16 (s, 3H, CH$_3$ *p*-tolyl); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 136.45, $\delta_B$ 44.63, $J_{AB}$ = 53.52; AB spin syst., $\delta_A$ 136.21, $\delta_B$ 44.52, $J_{AB}$ = 53.52; AB spin syst., $\delta_A$ 135.66, $\delta_B$ 44.05, $J_{AB}$ = 53.47 Hz; $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 165–122 (m, Ph + C4, C6 Tp), 127.0, 126.3 (br, CN), 107.03, 106.97, 106.88, 106.75, 106.71 (s, C5 Tp), 52.96, 52.93, 52.91 (d, CH$_3$ phos), 40.7, 39.9 (br, C3 pz), 22.81, 22.61, 22.14 (s, C4 or C5 pz), 21.25, 21.20, 21.05 (s, CH$_3$ *p*-tolyl), 13.79, 13.68, 13.66, 13.62 (s, C4 or C5 pz); Anal. Calcd for C$_{71}$H$_{69}$B$_2$N$_9$O$_3$P$_2$Ru (1281.01): C, 66.57; H, 5.43; N, 9.84; Found: C, 66.41; H, 5.50; N, 9.73%; $\Lambda_M$ = 52.1 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**3c**: IR (KBr, cm$^{-1}$) $\nu_{BH}$ 2482 (w), $\nu_{CN}$ 2235 (w); $^1$H NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 7.87–6.24 (m, 43H, Ph), 8.03, 7.93, 7.77, 7.68 (br, 3H, H3 Tp), 7.60, 7.23, 6.98, 6.49 (br, 3H, H5 Tp), 6.17, 6.14, 5.84, 5.77 (br, 3H, H4 Tp); **A**: ABC spin syst. (3H, CH$_2$CH pz), $\delta_A$ 2.37, $\delta_B$ 2.08, $\delta_C$ 1.56, $J_{AB}$ = −9.3, $J_{AC}$ = 7.2, $J_{BC}$ = 6.0, ABC spin syst., $\delta_A$ 2.47, $\delta_B$ 2.26, $\delta_C$ 2.18, $J_{AB}$ = −9.4, $J_{AC}$ = 7.4, $J_{BC}$ = 5.8; **B**: ABC spin syst., $\delta_A$ 2.26, $\delta_B$ 2.22, $\delta_C$ 2.06, $J_{AB}$ = 8.5, $J_{AC}$ = 5.5, $J_{BC}$ = −6.2 Hz; 3.33, 3.06 (d, 9H, CH$_3$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: AB spin syst., $\delta_A$ 135.55, $\delta_B$ 44.26, $J_{AB}$ = 53.47, AB spin syst., $\delta_A$ 135.50, $\delta_B$ 44.23, $J_{AB}$ = 54.47 Hz; $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 165–119 (m, Ph + C3 and C4 Tp), 125.85, 125.25 (s, CN), 107.2, 106.8, 105.3 (s, C5 Tp), 53.37 (d, $J_{CP}$ = 14), 53.00 (d, $J_{CP}$ = 24) (CH$_3$ phos), 36.89, 36.75 (s, C3 pz), 21.77, 21.75 (d, $J_{CP}$ = 12), 15.84, 15.79 (d, $J_{CP}$ = 4) (C4 or C5 pz); Anal. Calcd for C$_{70}$H$_{65}$B$_2$N$_9$O$_3$P$_2$Ru (1264.96): C, 66.46; H, 5.18; N, 9.97; Found: C, 66.28; H, 5.10; N, 10.07%; $\Lambda_M$ = 53.5 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**[Ru(bpza)(N$_2$CAr1Ar2)(PPh$_3$)$_2$]BPh$_4$ (4) [Ar1 = Ph, Ar2 = *p*-tolyl (b); Ar1Ar2 = C$_{12}$H$_8$ (c)].** In a 25 mL three-necked round-bottom flask were placed solid samples of RuCl(bpza)(PPh$_3$)$_2$ (300 mg, 0.33 mmol), an excess of NaBPh$_4$ (0.6 mmol, 205 mg), an excess of the appropriate diazoalkane (1.0 mmol), 8 mL of dichloromethane and 4 mL of ethanol. The reaction mixture was stirred for 24 h and then the solvent(s) removed under reduced pressure. The green solid obtained was treated with ethanol (2 mL), filtered and crystallised from CH$_2$Cl$_2$ and EtOH; yield ≥75%.




**4b**: IR (KBr, cm$^{-1}$) $\nu_{N_2}$ 1900 (m), $\nu_{CO}$ 1672 (s); $^1$H NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 7.40–6.58 (m, 59H, Ph), 7.42 (d, $J_{HH}$ = 2.3, 2H, H3 bpza), 6.68 (s, 1H, CH bridging bpza), 6.23 (d, $J_{HH}$ = 2.1, 2H, H5 bpza), 5.81 (t, $J_{HH}$ = 2.4 Hz, 2H, H4 bpza), 2.36 (s, 3H, CH$_3$); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: A$_2$ spin syst., 35.60 (s); $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 165–122 (m, Ph), 163.99 (s, COO$^-$), 146.07 (s, C5 bpza), 134.93 (s, C3 bpza), 109.11 (s, C4 bpza), 88.44 (s, CN$_2$), 75.10 (s, CH bridging bpza), 21.29 (s, CH$_3$); Anal. Calcd for C$_{82}$H$_{69}$BN$_6$O$_2$P$_2$Ru (1344.29): C, 73.26; H, 5.17; N, 6.25; Found: C, 73.43; H, 5.04; N, 6.12%; $\Lambda_M$ = 51.6 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

**4c**: IR (KBr, cm$^{-1}$) $\nu_{N_2}$ 1959 (m), $\nu_{CO}$ 1669 (s); $^1$H NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: 8.39–6.60 (m, 60H, Ph + H3 bpza), 6.73 (s, 1H, CH bridging bpza), 6.54 (d, $J_{HH}$ = 2.0 Hz, 2H, H5 bpza), 5.92 (br, 2H, H4 bpza); $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 20 °C) $\delta$: A$_2$ spin syst., 34.29 (s); Anal. Calcd for C$_{81}$H$_{65}$BN$_6$O$_2$P$_2$Ru (1328.25): C, 73.24; H, 4.93; N, 6.33; Found: C, 73.05; H, 5.01; N, 6.44%; $\Lambda_M$ = 53.3 Ω$^{-1}$ mol$^{-1}$ cm$^2$.

### Crystal structure determination

Crystallographic data were collected at room temperature using a Bruker Smart 6000 CCD detector and Cu-Kα radiation ($\lambda$ = 1.54178 Å) generated by an Incoatec microfocus source equipped with Incoatec Quazar MX optics. The software APEX2[30] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[30] for integration of the intensity of reflections, and SADABS[30] for scaling and empirical absorption correction. The crystallographic treatment was performed with the Oscail program.[31] The structure was solved by charge flipping in arbitrary dimensions (Superflip program)[32] and refined by a full-matrix least-squares based on $F^2$.[33] The Squeeze program[34] was used to correct the reflection data for the diffuse scattering due to the disordered molecules present in the unit cell. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Details of crystal data and structural refinement are given in Table 3. CCDC 1404716 contains the supplementary crystallographic data for this paper.

Table 3 Crystal data and structural refinement for **1b**

| | |
|---|---|
| Empirical formula | $C_{68}H_{66}B_2N_8O_3P_2Ru$ |
| Moiety formula | $C_{44}H_{46}BN_8O_3P_2Ru$, $C_{24}H_{20}B$ |
| Formula weight | 1227.91 |
| Temperature | 296(2) K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | $a$ = 9.8284(5) Å |
| | $b$ = 17.4110(8) Å |
| | $c$ = 19.4494(9) Å |
| | $\alpha$ = 89.2778(18)° |
| | $\beta$ = 77.1894(17)° |
| | $\gamma$ = 79.0992(18)° |
| Volume | 3185.3(3) Å$^3$ |
| $Z$ | 2 |
| Density (calculated) | 1.280 Mg m$^{-3}$ |
| Absorption coefficient | 2.875 mm$^{-1}$ |
| $F$(000) | 1276 |
| Crystal size | 0.163 × 0.060 × 0.055 mm |
| $\Theta$ Range for data collection | 2.331 to 68.576° |
| Index ranges | $-10 \leq h \leq 11$ |
| | $-20 \leq k \leq 20$ |
| | $-23 \leq l \leq 23$ |
| Reflections collected | 50 476 |
| Independent reflections | 11 258 [$R$(int) = 0.0837] |
| Completeness to $\theta$ = 67.679° | 97.0% |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7530 and 0.5261 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 11 258/0/761 |
| Goodness-of-fit on $F^2$ | 1.071 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1$ = 0.0513 |
| | w$R_2$ = 0.1327 |
| $R$ indices (all data) | $R_1$ = 0.0627 |
| | w$R_2$ = 0.1404 |
| Largest diff. peak and hole | 1.635 and −0.541 e Å$^{-3}$ |

### Computational details

The computational geometry optimization of the complexes was carried out without symmetry constraints, using the hyper-DFT M06 functional[35] and the range-separated ωB97X DFT functional[36] in combination with a polarized split-valence basis set composed by the 6-31G(d,p) set on the light atoms and the ECP-based LANL2TZ(f) set on the ruthenium centre.[37] The "restricted" formalism was applied in all the cases.[38] All the computational optimizations were performed on an Intel-based x86-64 workstation and the software used was Gaussian 09.[39]

## Acknowledgements

The authors would like to thank the CACTI, Universidade de Vigo, for X-ray data collection. Thanks are also due to Daniela Baldan, of the Università Ca' Foscari Venezia (Italy), for technical assistance.

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