This article is published as part of the Dalton Transactions themed issue entitled:

Dalton Transactions 40th Anniversary

Guest Editor Professor Chris Orvig, Editorial Board Chair University of British Columbia, Canada

Published in issue 40, 2011 of Dalton Transactions



Image reproduced with permission of Shinobu Itoh

Welcome to issue 40 of the 40th volume of Dalton Transactions-40/40! Articles in the issue include:

PERSPECTIVE:

Synthesis and coordination chemistry of macrocyclic ligands featuring NHC donor groups

Peter G. Edwards and F. Ekkehardt Hahn *Dalton Trans.*, 2011, 10.1039/C1DT10864F

FRONTIER:

<u>The future of metal–organic frameworks</u> Neil R. Champness *Dalton Trans.*, 2011, DOI: 10.1039/C1DT11184A

ARTICLES:

Redox reactivity of photogenerated osmium(II) complexes Jillian L. Dempsey, Jay R. Winkler and Harry B. Gray *Dalton Trans.*, 2011, DOI: 10.1039/C1DT11138H

<u>Molecular squares, cubes and chains from self-assembly of bis-bidentate bridging ligands with</u> <u>transition metal dications</u> Andrew Stephenson and Michael D. Ward *Dalton Trans.*, 2011, DOI: 10.1039/C1DT10263J

Visit the *Dalton Transactions* website for more cutting-edge inorganic and organometallic research <u>www.rsc.org/dalton</u>

Dalton Transactions

Cite this: Dalton Trans., 2011, 40, 10503

PAPER

The use of 1,2-dipiperidinoacetylene for the preparation of monometallic diaminoacetylene and homo- or heterobimetallic diaminodicarbene ruthenium(II) complexes*

Alex R. Petrov, Thomas Bannenberg, Constantin G. Daniliuc, Peter G. Jones and Matthias Tamm*

Received 8th April 2011, Accepted 21st June 2011 DOI: 10.1039/c1dt10606f

The reaction of the ynediamine 1,2-dipiperidinoacetylene (1) with $[(\eta^2 - COE)Cr(CO)_5]$, $[(THF)W(CO)_5]$ and $[RuCl_2(n^6-cymene)]_2$ afforded homobimetallic complexes 2a, 2b and 3, in which the diaminoacetylene 1 acts as a bis(aminocarbene) ligand by bridging two complex fragments $Cr(CO)_5$ (in **2a**), W(CO)₅ (in **2b**) and RuCl₂(η^6 -cymene) (in **3**). The reaction of **1** with [RuCl₂(PPh₃)₃] gave *trans*-[(1)RuCl(PPh₃)₂]Cl, [4]Cl, in which the alkyne 1 coordinates as a 4-electron donor ligand. The cation 4 represents a rare example of a square-planar Ru(II) complex with a low-spin ground state (S = 0), and its stability can be ascribed to the strong alkyne-metal π -interaction as confirmed by DFT calculations. Treatment with one or two equivalents of NaBPh₄ in acetonitrile gave [4]BPh₄ and the dicationic $[(1)Ru(PPh_3)_2(CH_3CN)_2](BPh_4)_2$, $[5](BPh_4)_2$, [4]Cl can be used for the preparation ofheterobimetallic Ru-Pd bis(aminocarbene) complexes by reaction with [(MeCN)₂PdCl₂], resulting in the formation of bimetallic $\mathbf{6}$ and tetrametallic $\mathbf{7}$.

Introduction

The majority of transition metal diaminoacetylene complexes of the type $[(\eta^2 - R_2 NC \equiv CNR_2)M]$ have been prepared by template methods that involve the formation of the C-C triple bond at the metal atom by coupling of adjacent isocyanide and/or aminocarbyne ligands.¹⁻⁴ In the resulting early transition metal complexes (M = Nb, Mo, W, Re), the diaminoacetylene ligand was shown to act usually as a four-electron donor with substantial contributions of "dicarbenoid" mesomeric structures such as B-D (Scheme 1). Naturally, these diaminodicarbene characteristics become even more pronounced in bimetallic complexes, as indicated by the resonance forms E-G, and the first bis(aminocarbene) complexes of this type were also obtained by indirect methods through reductive C-C coupling of cationic Fischer carbyne complexes such as $[Et_2NC = M(CO)_5]BF_4$ (M = Cr, W).⁵

In contrast, free diaminoacetylenes (ynediamines) have been only rarely employed for metal complexation, and to the best of our knowledge, the reaction of Fe(CO)5 with Me2NC=CNMe2 to afford $[(\eta^2-Me_2NC \equiv CNMe_2)Fe(CO)_3]$ via a ferracyclobutenone complex represents the only example of the formation of a mononuclear metal complex by coordination of an authentic



Scheme 1 Selected mesomeric structures for monometallic diaminoacetylene (A-D) and bimetallic (E-G) diaminodicarbene complexes.

diaminoacetylene.⁶ On rare occasions, bimetallic metal complexes have also been reported, and the CO substitution reaction between $[(\eta^5-C_5H_5)M(CO)_3]_2$ (M = Mo, W) and Et₂NC=CNEt₂ afforded [{ $(\eta^5-C_5H_5)M(CO)_2$ }_2(μ - η^1 : η^1 -Et₂NC=CNEt₂)], in which the presence of a metal-metal bond allows a formal description of these complexes as 1,2-dimetalacyclobuta-2,4-dienes and thus as dimeric carbyne complexes.7 Finally, it should be noted that a ditungsten dicarbene complex was isolated in low yield as a side product from the reaction of [(CO)₅W=C(Ph)H] with $Me_2NC \equiv CNMe_2$ by substitution of the alkylidene moiety,⁸ and the resulting complex, in which the alkyne ligand is bridging two $W(CO)_5$ units, is closely related to those obtained by reductive dimerization of cationic Fischer carbyne complexes (vide supra).5

Evidently, the coordination chemistry of diaminoacetylenes is comparatively poorly developed, which can be ascribed to the high reactivity of these electron-rich compounds and to the lack of reliable and adaptable synthetic protocols,⁹ although the preparation

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Hagenring 30, D-38106, Braunschweig, Germany. E-mail: m.tamm@tu-bs.de; Fax: (+49) 531-391-5387; Tel: (+49) 531-391-5309 † Electronic supplementary information (ESI) available: Details of the electronic structure calculations and presentations of all calculated structures together with Cartesian coordinates of their atomic positions are provided. CCDC reference numbers 819865-819872. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10606f

	C1–C2	C1–N1	C2-N2	C1-C2-N2	C2C1N1	
1 <i>ª</i>	1.206(2) 1.357(2)		1.359(2)	177.87(14)	173.92(14)	
1 ^b	1.221	1.351	1.352	177.8	177.4	
2a	1.468(2)	1.315(2)	1.318(2)	117.28(13)	116.90(13)	
2b	1.484(3)	1.306(3)	1.315(3)	116.7(2)	117.4(2)	
3 ^c	1.508(4)	1.307(2)	_	115.88(16)	_	
4^{d}	1.399(2)	1.301(2)	1.303(2)	146.27(15)	147.23(15)	
4 ^e	1.404(2)	1.298(2)	1.303(2)	148.11(15)	146.56(16)	
4⁄	1.388	1.316	1.312	148.4	148.4	
	1.405	1.328	1.322	148.8	148.1	
	1.405	1.318	1.313	146.3	147.5	
5	1.427(3)	1.299(3)	1.309(3)	144.3(2)	139.7(2)	
6	1.463(9)	1.330(7)	1.273(9)	123.8(5)	117.6(5)	
7	1.485(4)	1.311(4)	1.297(4)	121.9(3)	116.6(3)	

Table 1 Selected bond lengths (Å) and angles (°) for the diaminoalkyne moiety in complexes 2-7

^{*a*} Experimental values taken from ref. 12 for 1,2-di(4methylpiperidino)acetylene. ^{*b*} Calculated values at the MP2/cc-pVTZ level of theory. ^{*c*} Centrosymmetric structure. ^{*d*} In [4]Cl. ^{*e*} In [4]BPh₄. ^{*f*} Values for the M06-L (top), BP86 (middle) and B3LYP (bottom) functionals.

of the first ynediamine, 1,2-di-(diethylamino)acetylene, from 1,1dichloro-2-fluoroethylene was reported as long ago as 1964 by Viehe and Reinstein.¹⁰ Stimulated by our interest in the chemistry of diaminocyclopropenylidenes,¹¹ we have recently published a novel and simple synthetic methodology that relies on a Fritsch– Buttenberg–Wiechell (FBW) rearrangement upon monolithiation of 2,2-dibromo-1,1-ethenediamines and allows for the preparation of aromatic and aliphatic ynediamines with a variable substitution in high yield.^{12,13} Moreover, we were able to establish the first Xray crystal structures of diaminoacetylenes, which show almost perpendicular orientations of the NC₃ planes. With these alkynes at hand, we present here the first reports of their coordination chemistry, with particular emphasis on the ability of these ligands to act either as chelating or bridging ligands in mono- or bimetallic transition metal complexes, respectively.

Results and Discussion

Preparation of homobimetallic diaminodicarbene complexes

1,2-Dipiperidinoacetylene (1) was the alkyne of choice for the present study,¹² and its reaction with two equivalents of the Cr(CO)₅ transfer reagent $[(\eta^2-\text{COE})\text{Cr}(\text{CO})_5]$ (COE = *cis*cyclooctene)¹⁴ afforded the chromium complex $[(1){\text{Cr}(\text{CO})_5}_2]$ (**2a**), which could be isolated as a yellow, crystalline solid in 89% yield after redissolution and filtration through alumina (Scheme 2). The ¹³C NMR spectrum of **2a** (in C₆D₆) exhibits three low-field resonances at 216.9, 221.9 and 249.3 ppm, which can be assigned to the *cis*-CO, *trans*-CO and Cr=*C*-N carbon atoms, respectively, indicating that a bis(aminocarbene) complex has formed.¹⁵ The molecular structure was additionally established by X-ray diffraction analysis (Fig. 1, Table 1), confirming that the alkyne bridges two Cr(CO)₅ moieties in a dicarbenoid fashion.

The structural parameters are very similar to those reported for the analogous diethylamino-substituted dicarbene complex, which had been prepared by reduction of the carbyne complex $[Et_2NC = M(CO)_5]BF_4.^5$ For the latter complex, which displays crystallographic C_2 -symmetry, a comparatively long Cr–C_{carbene} bond length of 2.190(7) Å had been reported, which is in good



Fig. 1 ORTEP diagram of 2a with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°) in 2a (M = Cr)/2b (M = W): M1–C1 2.167(2)/2.316(2), M2–C2 2.208(2)/2.277(2), M1–C_{trans} 1.856(2)/1.985(3), \emptyset M1–C_{cis} 1.906(2)/2.039(3), M2–C_{trans} 1.856(2)/1.987(3), \emptyset M2–C_{cis} 1.907(2)/2.040(3), C1–C2 1.468(2)/1.484(3), C1–N1 1.315(2)/1.306(3), C2–N2 1.318(2)/1.315(3); C1–M1–C_{trans} 174.9(1)/173.0(1), C1–M1–C_{cis} 87.4(1)–96.3(1)/84.7(1)–100.8(1), C2–M2–C_{trans} 173.8(1)/175.2(1), C2–M2–C_{cis} 85.3(1)–100.4(1)/87.8(1)–96.4(1), C1–C2–N2 117.3(1)/116.7(2), C2–C1–N1 116.9(1)/117.4(2), N1–C1–C2–N2 93.2(2)/93.8(3).



Scheme 2 Synthesis of diaminodicarbene complexes.

agreement with the values of 2.167(1) and 2.208(2) Å determined for **2a**. Likewise, the two aminocarbene moieties are oriented in an almost perpendicular fashion as indicated by an N1–C1–C2–N2 torsion angle of 93.2(2)° and by an angle of 95.7° between the Cr1– C1–N1–C2 and Cr2–C2–N2–C1 planes. This orientation rules out any π -conjugation between the two adjacent aminocarbene fragments, and the C1–C2 distance of 1.468(2) Å complies with the presence of a C(sp²)–C(sp²) single bond.¹⁶ For comparison, the molecular structure of the isomorphous tungsten complex **2b** was also established by X-ray diffraction analysis (see ESI for experimental details†); its structural parameters (Fig. 1, Table 1) are in good agreement with those reported for the analogous ditungsten complex containing Me₂NC=CNMe₂ as a bridging bis(aminocarbene) ligand.⁵

The alkyne **1** was also reacted with bimetallic $[RuCl_2(\eta^6-cymene)]_2$,¹⁷ since this compound has been successfully employed for the preparation of numerous ruthenium half-sandwich complexes containing *N*-heterocyclic carbenes.¹⁸ A few brick-red crystals of the dicarbene complex **3** were isolated from benzene solution, allowing the determination of its X-ray crystal structure

(Fig. 2). Unfortunately, we were unable to obtain 3 in sufficient quantity and purity for conclusive analytical and spectroscopic characterization, which could be attributed to the high lability of the cymene moiety in 3 and further agglomeration reactions as reported for similar systems.¹⁹ Nevertheless, the structure of **3** is discussed herein, since it provides evidence for the ability of the alkyne ligand 1 to bridge two Ru atoms, in contrast to the coordination to one Ru atom in a chelating fashion as observed below. In the solid state, complex 3 exhibits crystallographic C_2 -symmetry with two structurally identical [RuCl₂(η^6 -cymene)] units. Similar to complexes 2, the orientation of the two aminocarbene moieties is close to orthogonality as indicated by an interplanar angle of 83.0° together with a N-C1-C1'-N1' torsion angle of 81.2(3)° (Table 1). The Ru-C1 distance is 2.097(2) Å, which falls in the range observed for related mono- and bimetallic complexes with carbenes coordinated to the cymene-RuCl₂ complex fragment.¹⁸



Fig. 2 ORTEP diagram of 3 in $3 \cdot C_6 H_6$ with thermal displacement parameters drawn at 50% probability. Primes indicate symmetry-equivalent atoms. Selected bond lengths (Å) and angles (°):Ru–C1 2.097(2), Ru–Cl1 2.417(1), Ru–Cl2 2.414(1), Ru–C_{cymene} 2.172(2)–2.283(2), C1–C2 1.508(4), C1–N1 1.307(2); C1–Ru–Cl1 88.3(1), C1–Ru–Cl2 87.5(1), C11–Ru–Cl2 87.5(1), C11–C2–N 115.9(2), N–C1–C1'-N' 81.2(3).

Preparation of monometallic diaminoacetylene complexes

Although ruthenium η^2 -alkyne complexes represent important intermediates in numerous organic transformations and are involved in alkyne/vinylidene and alkyne/allenylidene interconversions,^{20,21} they have only been isolated in a limited number of cases.²² Aiming at the synthesis of a ruthenium complex containing a η^2 -bound diaminoacetylene ligand, the reactivity of 1 towards [RuCl₂(PPh₃)₃] was investigated, since this complex and also related Grubbstype complexes readily undergo phosphine exchange reactions.^{23,24} Hence, addition of 1 to a suspension of this complex in THF at low temperature (-20 °C) led to an immediate formation of a deep-green solution. Upon warming to ambient temperature, the colour of the reaction mixture gradually turned maroon, and a purple, microcrystalline solid precipitated (Scheme 3). These colour changes indicate that various intermediate species are

presumably formed in the course of this reaction, e.g. by stepwise ligand substitution and rearrangement. Elemental analysis of the purple solid revealed that the isolated complex has the composition $[(1)RuCl_2(PPh_3)_2]$ THF; the solvent can be removed by extensive drying in vacuo. The resulting material is highly soluble in CH₂Cl₂ and MeCN, only marginally soluble in CHCl₃ and insoluble in ethers (THF, Et₂O) and hydrocarbons, implying an ionic nature. Recrystallization from chloroform solution afforded single crystals, and X-ray diffraction analysis revealed that the complex [(1)RuCl(PPh₃)₂]Cl·3CHCl₃ has formed, which is indeed composed of the cation $[(1)RuCl(PPh_3)_2]^+$ (4) and a solvated chloride counterion $[Cl(CHCl_3)_3]^-$ with $Cl \cdots H$ distances of 2.33-2.44 Å. The molecular structure of the cation 4 (Fig. 2) is best described as *pseudo*-square-planar with an almost perfectly perpendicular arrangement of the η^2 -bound diaminoacetylene ligand with regard to the P1-Ru-P2 axis. The Cl-Ru-P angles are $88.00(1)^\circ$ and $87.43(1)^\circ$, indicating that the phosphine ligands are slightly tilted towards the chlorine atom (Fig. 3).



Fig. 3 ORTEP diagram of 4 in [4]Cl·3CHCl₃ with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°) in [4]Cl/[4](BPh₄): Ru–Cl 1.9188(15)/1.9265(16) Ru–C2 1.9215(15)/1.9174(16), Ru–Cl 2.3840(4)/2.3856(4), Ru–P1 2.3836(4)/2.3839(4), Ru–P2 2.3890(4)/2.3959(4), C1–C2 1.399(2)/1.404(2), C1–N1 1.301(2)/1.298(2), C2–N2 1.303(2)/1.303(2); P1–Ru–P2 175.42(1)/174.48(1), P1–Ru–Cl 88.0(1)/86.25(1), P2–Ru–Cl 87.43(1)/89.29(1), C1–C2–N2 146.3(2)/148.1(2), C2–C1–N1 147.2(2)/146.6(2).

The most important structural feature is the observation of a long C1–C2 bond of 1.399(2) Å, which is significantly longer than usually observed in alkyne complexes²⁵ and is also among the longest reported for diaminoacetylene complexes;^{1-4,6} for instance, the corresponding C–C bond length in [(η^2 -Me₂NC==CNMe₂)Fe(CO)₃] was reported to be 1.375(4) Å.⁶ This C–C bond elongation is associated with short N–C_{alkyne} and Ru–C bond lengths of 1.301(2)/1.303(2) Å and 1.9188(15)/1.9215(15) Å, respectively, which strongly suggests the presence of a fourelectron alkyne ligand with ligand-to-metal σ - and π -donation and with extensive π -electron delocalization as described in Scheme 1 by the resonance structures **B–D**.²⁵ Accordingly, the cation **4** can reliably be regarded as a 16-electron complex.



Scheme 3 Synthesis of monometallic diaminoacetylene and heterobimetallic diaminodicarbene complexes; for compounds 6 and 7, the drawings refer to the stereoisomers depicted in Fig. 6 and 7.

The ¹H NMR spectrum shows two multiplets for the α -CH₂groups, in agreement with the expected restricted rotation of the piperidyl groups around the N–C $_{alkyne}$ axis, which is also confirmed by the observation of two sets of ¹³C NMR resonances each for the α - and β -CH₂ carbon atoms. Upon coordination, a very large low-field shift is observed for the C=C resonance from 74.8 ppm in the free alkyne 1¹² to 203.1 ppm in [4]Cl. The latter resonance appears as a triplet because of coupling with the two phosphorus nuclei (${}^{2}J_{CP} = 8.5$ Hz). It should be noted that the position and the shape of all NMR resonances are fully consistent with the presence of a diamagnetic species with a stable lowspin configuration, e.g. the ³¹P NMR resonance at +31.6 ppm is sharp ($\Delta v_{1/2} = 3.1$ Hz) and shows no temperature dependence. In contrast, the NMR data of the recently reported pincer complex [(PNP)RuCl] [PNP = N(CH₂CH₂PtBu₂)₂], which represents an unprecedented example of a square-planar Ru(II) complex with a low-spin (LS) ground state (S = 0),²⁶ suggested the presence of an energetically low-lying intermediate-spin (IS) excited state (S = 1)²⁷ For the latter complex, the stability of the electronic LS configuration was attributed to a combination of steric bulk and the strong nitrogen-to-metal π -donation from the chelating amido ligand. Accordingly, the high stability of the diamagnetic squareplanar arrangement in 4 can also be explained by the effective π interaction between the metal and the four-electron alkyne ligand (vide supra).

These assumptions are supported by a series of DFT calculations, whereby the geometry of the cation **4** was freely optimized in the singlet (S = 0) and triplet state (S = 1) employing different functionals (B3LYP, BP86 and M06-L). In all cases, the calculated structures of the singlet state are in good agreement with those determined by X-ray diffraction analysis (Table 1, see also Supplementary Information), whereas longer metal–ligand distances are derived for the triplet state structures. The calculated energy gap between the singlet and triplet states is of the same order of magnitude for all three functionals with $\Delta E_{s-T} = -22.1$ (B3LYP), -27.4 (BP86) and -22.6 kcal mol⁻¹ (M06-L), respectively. In agreement with the spectroscopic results, this gap is much larger than calculated for the pincer complex [(PNP)RuCl] [PNP = $N(CH_2CH_2PtBu_2)_2$ (vide supra), for which the small separation of $\Delta E_{\text{s-T}} = +2.3$ (B3LYP) and -2.0 kcal mol⁻¹ (BP86), derived at the same level of theory, did not allow a reliable theoretical assignment of the electronic ground state.27 Together with the experimental data, however, these calculations are in agreement with a singlet ground state for this complex, whereas related square-planar pincer complexes of the type $[RuX{N(SiMe_2CH_2PtBu)_2}]$ (X = F, Cl, OTf) exhibit triplet (IS) ground-state configurations.²⁸ As already deduced from the structural characteristics of 4 (vide supra), the exceedingly strong stabilization of its diamagnetic ground state arises from an efficient ligand-to-metal π -donation, which increases the energy of the lowest unoccupied molecular orbital (LUMO) in comparison with the above-mentioned pincer complexes, which contain more weakly π -donating amido-units. Accordingly, the LUMO represents the antibonding alkyne-metal π^* -combination involving the π_{\perp} alkyne orbital and the d_{xv} metal orbital (with the square around the Ru atom being defined as the xy plane),^{25,29} whereas the highest occupied molecular orbital (HOMO) exhibits the expected pronounced metal d_{r^2} character (Fig. 4).^{26,27}



Fig. 4 Contour plots of the HOMO (left) and LUMO (right) in the cation **4** (singlet state); CH and CH₂ groups were partially omitted for clarity.

The chloride counterion in [4]Cl can be easily exchanged, and treatment with one equivalent of NaBPh4 in acetonitrile resulted in the formation of [4]BPh₄ (Scheme 3). The spectroscopic data of the cation 4 in the BPh₄-salt are virtually identical with those in the chloride congener, and an X-ray diffraction analysis confirmed the presence of a square-planar cation 4 with almost identical structural features (see caption of Fig. 3, Table 1). The same reaction with two equivalents of NaBPh₄ allows the additional removal of the coordinated chloride ion to afford a crystalline amber-colored solid, which was identified as $[(1)RuCl(PPh_3)_2(CH_3CN)_2](BPh_4)_2$, $[5](BPh_4)_2$, by elemental and X-ray diffraction analysis (Scheme 3). The molecular structure of the dication 5 is shown in Fig. 5, revealing that two acetonitrile ligands are bound to the Ru atom in a cis-fashion and are coplanar with the alkyne ligand. Since the P-Ru-N and the N-Ru-N angles are all close to 90°, the coordination sphere around the Ru atom is probably best described as *pseudo*-octahedral, with the alkyne ligand formally occupying two coordination sites. The structural parameters of the coordinated diaminoacetylene ligand are again completely consistent with the alkyne acting as a four-electron donor ligand and thus comply with an 18-electron count for 5; the C1–C2 bond length of 1.427(3) Å in the dication 5 is even longer than those established for the monocations in [4]Cl and [4]BPh₄ (Table 1). As expected, similar NMR data are recorded for 5, and the resonances for the metal-bound carbon and phosphorus atoms are observed at 210.7 (${}^{2}J_{PC} = 8.4 \text{ Hz}$) and +35.8 ppm, respectively, slightly downfield from the resonances of 4.



Fig. 5 ORTEP diagram of 5 in [5](BPh₄)₂·0.5CH₃CN with thermal displacement parameters drawn at 50% probability. Selected bond lengths (Å) and angles (°):Ru–C1 1.959(2), Ru–C2 1.922(2), Ru–N3 2.159(2), Ru–N4 2.120(2), Ru–P1 2.4059(6), Ru–P2 2.4291(6), C1–C2 1.427(3), C1–N1 1.299(3), C2–N2 1.309(3); P1–Ru–P2 173.2(1), N3–Ru–N4 83.7(1), P1–Ru–N3 85.3(1), P1–Ru–N4 91.3(1), P2–Ru–N3 87.9(1), P2–Ru–N4 88.8(1), C1–C2–N2 144.3(2), C2–C1–N1 139.7(2), N1–C1–C2–N2 17.7(6).

Preparation of heterobimetallic diaminodicarbene complexes

The ability of the alkyne **1** to act as a chelating diaminoacetylene ligand towards a single metal or as a bridging diaminodicarbene ligand towards two metals suggested that complex **[4]**Cl might serve as a starting material for the preparation of heterobimetallic

complexes, since the addition of other metal cations could lead to a bridging dicarbene ligand with reincorporation of the chloride counterion into the coordination sphere. Therefore, the reaction of [4]Cl with [(MeCN)₂PdCl₂] was investigated (Scheme 3). Optimization of the reaction conditions indicated that 1.5 equivalents of the palladium(II) reagent were required to obtain an authentic reaction product, and the reaction in CH₂Cl₂ resulted in immediate precipitation of $[PdCl_2(PPh_3)_2]$, which serves as a triphenyl phosphine scavenger.³⁰ Filtration and recrystallization of the reaction product from acetonitrile afforded orange needles in 70% yield. Xray diffraction analysis revealed that a heterobimetallic complex 6 had indeed formed, in which a ruthenium and a palladium atom are bridged by a chloro ligand and by the alkyne 1 acting as a bis(aminocarbene) ligand (Fig. 6). The Pd atom resides in a square-planar environment composed of the carbene ligand, one bridging and two terminal chlorine atoms, whereas the Ru atom is coordinated in an octahedral fashion by the carbene and only one PPh₃ ligand, a bridging and a terminal chlorine atom and two cis-coordinated CH₃CN ligands. The ¹H NMR spectrum is rather complicated, in particular in the aliphatic region because of the low symmetry of the complex, but unambiguously confirms the presence of only one PPh₃ ligand per Ru atom; however, the low solubility of 6 did not allow to obtain a conclusive ¹³C NMR spectrum. The ³¹P NMR resonance is found at +49.5 ppm, which is downfield from the signals observed for the cations 4 and 5.



Fig. 6 ORTEP diagram of 6 in 6.7CH₃CN with thermal displacement parameters drawn at 30% probability. Selected bond lengths (Å) and angles (°): Ru–C1 2.041(6), Ru–Cl1 2.478(1), Ru–Cl2 2.418(2), Ru–N3 2.020(6), Ru–N4 2.108(5), Pd–C2 1.983(6), Pd–Cl1 2.314(2), Pd–Cl3 2.377(2), Pd–Cl4 2.315(2), C1–C2 1.463(9), C1–N1 1.330(7), C2–N2 1.273(9); P–Ru–Cl1 174.9(1), P–Ru–Cl2 86.9(1), N3–Ru–N4 85.6(2), C1–Ru–P 97.0(2), C1–Ru–Cl1 86.2(2), C1–Ru–Cl2 92.9(2); C11–Pd–Cl3 92.3(1), C11–Pd–Cl4 174.9(1), Cl3–Pd–Cl4 91.6(1), C2–Pd–Cl1 86.3(2), C2–Pd–Cl4 90.0(2), C1–C2–N2 123.8(5), C2–C1–N1 117.6(5).

The formation of complex **6** can be rationalized by the assumption that chloride exchange in an acetonitrile solution of [**4**]Cl delivers sufficient quantities of the dication **5**, which undergoes $PdCl_2$ insertion with concomitant chloride coordination and phosphine dissociation. The low solubility of $[PdCl_2(PPh_3)_2]^{29}$ and

also the inability of the bimetallic system to accommodate two PPh₃ ligands for steric reasons might provide the driving force for the latter process. Recrystallization of 6 from CH₂Cl₂ afforded orange crystals of different shape, which were identified as the tetranuclear complex 7 by an X-ray diffraction study (Scheme 3, Fig. 7). 7 can be regarded as a dimer of 6, and its formation involves dissociation of one CH₃CN ligand in 6 and association of the resulting coordinatively unsaturated complex fragments via the two bridging chlorine atoms Cl2 and Cl2'. It should be noted that the asymmetric unit of 7.4CH2Cl2 contains one molecule with inversion symmetry (in the centre of the four-membered Ru₂Cl₂ ring) and one molecule on a general position, but with approximate inversion symmetry (r.m.s. deviation 0.20 Å). The orientation of the ligands and the overall structural parameters in both molecules are very similar, and only those of the centrosymmetric molecule are discussed here (Fig. 7). The Ru-C and Pd-C distances in 7 [2.010(3), 1.951(3) Å] differ only slightly from those in 6 [2.041(6), 1.983(6) Å]; they fall in the range observed for other ruthenium(II)and palladium(II)-aminocarbene complexes.31,32

Fig. 7 ORTEP diagram of 7 in 7.4CH₂Cl₂ with thermal displacement parameters drawn at 50% probability. The asymmetric unit contains 1.5 molecules of 7, but only the structure of the centrosymmetric molecule is shown. The phenyl groups of the PPh₃ ligands were omitted for clarity. Selected bond lengths (Å) and angles (°):Ru-C1 2.010(3), Ru-P 2.313(1), Ru-Cl1 2.446(1), Ru-Cl2 2.470(1), Ru-Cl2 2.453(1), Ru-N3 1.995(3), Pd-C2 1.951(3), Pd-Cl1 2.332(1), Pd-Cl3 2.377(1), Pd-Cl4 2.305(1), C1-C2 1.485(4), C1-N1 1.311(4), C2-N2 1.297(4); C1-C2-N2 121.9(3), C2-C1-N1 116.6(3), C1-Ru-P 101.8(1), C1-Ru-Cl1 88.1(1), C1-Ru-Cl2'92.7(1), C1-Ru-Cl2 172.0(1), C1-Ru-N3 91.1(1); C2-Pd-Cl1 85.0(1), C2-Pd-Cl3 179.3(1), C2-Pd-Cl4 87.8(1), Cl1-Pd-Cl3 94.3(1), Cl3-Pd-Cl4 92.9(1).

The formation of the Ru-Pd complexes 6 and 7 from [4]Cl shows that this complex can serve as a starting material for the preparation of heterobimetallic diaminocarbene complexes. Originally, we anticipated that this reaction might formally proceed via a discribene intermediate of the type [{Ru}=C(NR₂)-(R₂N)C:] with $\{Ru\} = RuCl_2(PPh_3)_2$, followed by coordination of a bridiging PdCl₂ moiety; however, phosphine dissociation and ligand scrambling was observed. Although we cannot provide evidence for the intermediate occurrence of such a dicarbene species at this time, the isolation of the cationic complex [(OC)₄Fe=C(NMe₂)-(Me₂N)CH]⁺ by Filippou might serve as an example of the trapping of a similar dicarbene complex by protonation.⁶ In future work, phosphine dissociation could be avoided by use of more strongly coordinating ligands such as trialkyl phosphines and N-heterocyclic carbenes and might therefore allow delivery of the ruthenium dicarbene complex in a more controlled fashion.

Conclusions

The present paper shows that ynediamines such as 1 can be used for the preparation of homobimetallic or monometallic diaminoacetylene complexes; in both systems, the alkyne ligand acts as a 4-electron donor either by bridging two metals as a bis(aminocarbene) ligand or by coordination to a single transition metal as a 2σ , 2π -electron donor. The latter behaviour was exemplified by isolation of the cationic pseudo-squareplanar Ru(II) complex trans-[(1)RuCl(PPh₃)₂]⁺ (4), which exhibits an unusual, very stable low-spin singlet ground state as a consequence of strong alkyne-to-metal π -donation. The monometallic complex 4 can be used for the preparation of heterobimetallic bis(aminocarbene) complexes, indicating that a controlled conversion between monometallic diaminoacetylene and bimetallic dicarbene complexes is possible. In that respect, the diaminoacetylene 1 might be regarded as a diaminodicarbene source and consequently as a conjoined bifunctional analogue of well-established alkyl-aminocarbenes such as $iPr_2N(tBu)C$: or their cyclic (CAAC) congeners.33

Experimental

General procedures

All manipulations, unless otherwise stated, were performed under inert gas atmosphere (Ar), using Schlenk and glovebox techniques. All solvents were purified by standard methods and degassed prior to use. ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectroscopic studies were carried out on Bruker DPX200, AV300 and Bruker DRX400 devices and were referenced to internal SiMe₄ (¹H, ¹³C) and to external H₃PO₄ (³¹P). Splitting patterns are indicated as s (singlet), d (doublet), t (triplet), m (multiplet) and pst (pseudotriplet). Elemental analyses were performed by combustion analysis on a Vario Micro Cube device with WLD and IR detectors. FTIR spectra were recorded using a Bruker Vertex 70 spectrometer equipped with a diamond ATR cell. The starting materials were prepared according to published procedures: [RuCl₂(PPh₃)₃],^{22a} $[(\eta^{6}\text{-cymene})\text{RuCl}_{2}]_{2}^{17}$ $[(THF)W(CO)_{5}]_{34}^{34}$ $[(\eta^{2}\text{-COE})Cr(CO)_{5}]_{34}^{14}$ [(MeCN)₂PdCl₂],³⁵ 1,2-dipiperidinoacetylene (1),¹² or purchased and used as delivered: (-)-p-mentha-1,5-diene (TCI Europe), [W(CO)₆] (Acros).

Synthesis and characterization of 2a

A solution of 1 (240 mg, 1.12 equiv.) in toluene (5 mL) was added to a solution of $[(\eta^2 - COE)Cr(CO)_5]$ (600 mg, 2.0 mmol) in 20 mL of the same solvent. The reaction mixture gradually turned deep yellow. After stirring for another 0.5 h, the volume was decreased by half and hexane (10 mL) was added, whereupon a yellow crystalline solid formed. It was isolated by filtration, washed twice with hexane (10 mL) and dried in vacuo. Further purification was achieved by filtration of its CH₂Cl₂ solution through a short Al₂O₃pad (Super I) and subsequent solvent removal. Yield: 89% (510 mg) of a bright yellow microcrystalline solid. ¹H NMR (200.1 MHz,





C₆D₆, 300 K): δ = 1.4–2.0 (m, 6H), 3.6 (m, 2H), 3.8, 4.8 (2 ×d, 2 × 1H, ²J_{HH} = 12 Hz, 2×α-CH₂) ppm. ¹³C NMR (50.1 MHz, C₆D₆, 300 K): δ = 23.4 (γ-CH₂), 26.7, 26.8 (2×β-CH₂), 57.6, 59.5 (2×*a*-CH₂), 216.9 (*cis*-CO), 221.9 (*trans*-CO), 249.3 (Cr=C-N) ppm. Anal. calc'd for C₂₂H₂₀Cr₂N₂O₁₀ (576.41): C 45.84, H 3.49, N 4.86; found C 45.45, H 3.56, N 4.91. IR: *v* 2957w, 2060 m, 2045 m, 1986 m, 1877 s, 1528 m, 1502 m, 1444 m, 1279 m, 1265 m, 1225 m, 1091 m, 1022 m, 861 m, 645 s cm⁻¹.

Synthesis of 2b

A suspension of $[W(CO)_6]$ (362 mg, 1.03 mmol) in THF (80 mL) was irradiated with UV light for 60 min under a slow flow of inert gas, affording a deep yellow solution. The reagent was transferred to a Schlenk flask, and the solution was concentrated *in vacuo* to half of the original volume and cooled to -20 °C. Upon addition of 1, the reaction mixture gradually turned deep orange. After overnight stirring, the solvent was completely evaporated, and the residue was additionally dried for 3 h (2 × 10⁻² mbar) at ambient temperature. Crystalline material was obtained upon storing a THF solution at 5 °C.

Synthesis and characterization of 3

A solution of 1 (130 mg, 0.68 mmol, 1.1 equiv.) in THF (3 mL) was added dropwise at -20 °C to a stirred suspension of [(η^6 -cymene)RuCl₂]₂ (380 mg, 0.62 mmol) in THF (10 mL), affording a deep orange reaction mixture. The clear reaction mixture was stirred for 30 min and subsequently concentrated in *vacuo* to *ca.* 2 mL. Upon addition of benzene (5 mL), slow precipitation of a deep red solid was observed. Precipitation was completed by dropwise addition of hexane (3 mL). The precipitate was isolated by filtration and dried *in vacuo* for 2 h (2 × 10⁻² mbar), affording 160 mg of a brown amorphous solid. NMR spectroscopic data in C₆D₆ indicate the presence of a very complex reaction mixture. All attempts to isolate an analytically pure compound failed. Several crystals of the composition 3 ·C₆H₆, suitable for X-ray diffraction analysis, were obtained by storing concentrated C₆H₆ solutions at 5 °C.

Synthesis and characterization of [4]Cl·THF

A suspension of [RuCl₂(PPh₃)₃] (1.92 g, 2.00 mmol) in THF (50 mL) was cooled to 0 °C, and a solution of 1 (404 mmol, 2.10 mmol) in THF (5 mL) was added, whereupon a brilliant deep-green solution formed. After 15 min of vigorous stirring, the reaction mixture was brought to ambient temperature without stirring. The solution gradually turned maroon, and a purple, amorphous solid precipitated. The solid was isolated by filtration, washed with THF $(3 \times 5 \text{ mL})$ and dried in vacuo (1 mbar, 60 min). Yield: 71% (1.36 g). NMR spectroscopy and elemental analysis reveal the presence of one THF molecule per formula unit. Extended drying at higher temperatures (>60 °C) led to an unsolvated material. Crystallization from hot CHCl₃ (100 mg/6 mL) resulted in the formation of the CHCl₃ solvate [4]Cl·3CHCl₃) as a brown, crystalline solid. [4]Cl·THF is highly soluble in CH₂Cl₂ and MeCN, marginally soluble in CHCl₃ and insoluble in ethers (THF, Et₂O) and hydrocarbons. ¹H NMR (400.1 MHz, CH₂Cl₂, 300 K): $\delta = 1.24$ (m, 4H, β/γ -CH₂), 1.46 (m, 2H, β -CH₂), 1.82 (m, 4H, THF), 2.95 (m, 2H, α-CH₂), 3.69 (m, 4H, THF), 4.00 (m,

2H, α -HCH_B), 7.41–7.60 (m, 3 × 5H, *Ph*) ppm. ¹³C{¹H} NMR (100.6 MHz, CH₂Cl₂, 300 K): δ = 23.1 (γ -CH₂), 25.7, 25.8 (2× β -CH₂), 25.9 (*THF*), 57.4, 59.0 (2× α -CH₂), 68.1 (*THF*), 129.0 (pst, ³J_{CP} = 5.0 Hz, *m*-*Ph*), 131.3 (s, *p*-*Ph*), 132.3 (pst, ¹J_{CP} = 22 Hz, *ipso*-*Ph*), 134.5 (pst, ²J_{CP} = 5.8 Hz, *o*-*Ph*), 203.1 (t, ²J_{CP} = 8.5 Hz, Ru=C) ppm. ³¹P{¹H} NMR (81.1 MHz, CH₂Cl₂, 300 K): δ = +31.6 ppm. Anal. calc'd for [4]Cl·THF, C₅₂H₅₈Cl₂N₂OP₂Ru (960.97): C 64.99, H 6.08, N 2.92; found: C 64.69, H 6.43, N 2.85.

Synthesis and characterization of [4]BPh₄·THF

To a solution of [4]Cl·THF (385 mg, 0.40 mmol) in MeCN (20 mL), solid NaBPh₄ (144 mg, 0.42 mmol, 1.05 equiv.) was added, and the resulting brown suspension was stirred vigorously for 30 min. The solid was filtered off, and all volatiles were evaporated. THF (10 mL) was added to the remaining brown foamy solid, and the solution was stored at -30 °C, affording a crystalline material. It was collected by decantation, washed with ether $(3 \times 5 \text{ mL})$ and dried in vacuo. Yield: 64% (321 mg) of a lustrous sand-colored solid of the composition [4]BPh₄·THF. The complex is highly soluble in polar solvents. Single crystals suitable for X-ray diffraction analysis were obtained upon storing a concentrated THF solution at 5 °C. ¹H NMR (300.1 MHz, CD₃CN, 300 K): $\delta = 1.17$ (br s, 2H, γ -CH₂), 1.45 (br s, 4H, 2× β -CH₂), 1.81 (m, 4H, THF), 2.74, 3.95 (2 × m, 2 × 2H, α -C(H)H), 3.65 (m, 4H, THF), 6.84 (t, ${}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 4\text{H}, p-Ph\text{B}), 6.99 \text{ (t, }{}^{3}J_{\text{HH}} = 7.2 \text{ Hz}, 8\text{H}, m-Ph\text{B}),$ 7.25-7.33 (m, 8H, o-PhB), 7.39-7.50 (m, 18H, m-/p-PhP) 7.61-7.71 (m, 12H, *o-PhP*) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₃CN, 300 K): $\delta = 23.5 (\gamma - CH_2)$, 26.1, 26.8 (2 × β -CH₂), 26.2 (THF), 58.9, 59.3 (2 ×α-CH₂), 68.3 (THF), 122.7 (s, p-PhB), 126.6 (m, ${}^{3}J({}^{13}\text{C}-{}^{11}\text{B}) = 2.7 \text{ Hz}, m-PhB), 129.3 \text{ (pst, } |{}^{3}J_{CP} + {}^{5}J_{CP'}| = 5.0 \text{ Hz},$ *m*-*Ph*P), 131.3 (s, *p*-*Ph*P), 132.2 (pst, $|{}^{1}J_{CP} + {}^{3}J_{CP'}| = 22.5$ Hz, *ipso-Ph*P), 135.0 (pst, $|{}^{2}J_{CP} + {}^{4}J_{CP'}| = 5.6$ Hz, *o-Ph*P), 136.7 (m, $^{2}J(^{13}C^{-11}B) = 1.3$ Hz, o-PhB), 164.8 (m, $^{1}J(^{13}C^{-11}B) = 50$ Hz, $^{1}J(^{1$ 10 B) = 16.7 Hz, *ipso-Ph*B), 199.7 (t, $^{2}J_{CP}$ = 8.4 Hz, Ru=C) ppm. ³¹P{¹H} NMR (81.0 MHz, CD₃CN, 300 K): δ = +32.1 ppm. Anal. calc'd for [4]BPh₄·THF, C₇₆H₇₈BClN₂OP₂Ru (1244.76): C 73.33, H 6.32, N 2.25; found: C 72.52, H 6.40, N 2.45.

Synthesis and characterization of [5](BPh₄)₂

Solid NaBPh₄ (320 mg, 0.96 mmol, 2.2 equiv) was added to a solution of [4]Cl·THF (420 mg, 0.44 mmol) in MeCN (20 mL), and the resulting brown suspension was stirred vigorously for 30 min. The solid was filtered off, and all volatiles were removed in vacuo. The remaining green-brown foamy solid was triturated with THF (8 mL), whereupon a sand-colored, microcrystalline solid formed. It was collected by decantation, washed with THF $(2 \times 4 \text{ mL})$ and dried in vacuo. Yield: 69% (470 mg). Complex [5](BPh₄)₂ is highly soluble in polar solvents (CH₂Cl₂, MeCN, acetone). Single crystals suitable for X-ray diffraction analysis were obtained upon storing a concentrated MeCN solution at ambient temperature. ¹H NMR (400.0 MHz, CD₃CN, 300 K): $\delta = 1.17$ (m, 2H, γ -CH₂), 1.51, 1.60 (2 × m, 2 × 2H, 2 × β -CH₂), 2.74, 3.93 (2 × t, ²J_{HH} = 6.0 Hz, 2×2 H, α -C(*H*)*H*), 6.82 (t, ${}^{3}J_{HH} = 7.2$ Hz, 4H, *p*-*Ph*-B), 6.79 (t, ${}^{3}J_{HH} = 7.2$ Hz, 8H, m-Ph-B), 7.25–7.30 (m, 8H, o-Ph-B), 7.40–7.52 (m, 15H, Ph_3P) ppm. ¹³C{¹H} NMR (100.6 MHz, CD₃CN, 300 K): δ = 1.7 (CH₃CN), 23.4 (γ -CH₂), 26.3 (β -CH₂), 60.1, 60.3 (2 ×α-CH₂), 79.2 (CHCl₃), 122.8 (s, *p*-Ph-B), 126.6 (m,

Table 2 Crystallographic data

	2a	2b	$3 \cdot \mathbf{C}_6 \mathbf{H}_6$	[4]Cl·3 CHCl ₃	[4] (BPh₄)·3 THF	5.0.5 MeCN	6.7 MeCN	$7{\cdot}4~CH_2Cl_2$
Empirical	$C_{22}H_{20}Cr_2N_2O_{10}$	$C_{22}H_{20}W_2N_2O_{10}$	$C_{38}H_{54}Ru_2N_2Cl_4$	$C_{51}H_{53}RuN_2$ -	$C_{84}H_{94}RuN_2P_2$ -	C _{100.99} H _{97.49} -	C ₄₈ H ₆₂ -	$C_{68}H_{84}Ru_2Pd_2$ -
formula				P_2Cl_{11}	ClBO ₃	$RuN_{4.49}P_2B_2$	$RuPdN_{11}PCl_4$	$N_6P_2Cl_{16}$
a/Å	9.4757(8)	9.5233(4)	17.3697(6)	14.3361(2)	14.3816(2)	11.6660(2)	9.5899(8)	17.1006(4)
b/Å	9.6051(6)	9.7656(4)	9.7250(2)	23.2191(2)	26.5861(2)	26.9068(6)	15.9641(18)	18.8239(4)
c/Å	15.9506(14)	15.9927(6)	22.3104(6)	17.3423(2)	18.6904(2)	26.0151(6)	17.390(2)	21.0090(6)
α (°)	103.107(6)	102.934(4)	90	90	90	90	80.429(9)	94.226(2)
β (°)	94.293(6)	94.073(4)	95.454(2)	107.837(2)	97.387(2)	97.058(2)	76.303(8)	110.213(2)
γ (°)	118.080(8)	118.147(4)	90	90	90	90	86.480(8)	98.865(2)
V (Å3)	1219.32(17)	1250.88(9)	3751.62(18)	5495.27(11)	7086.97(14)	8104.1(3)	2550.0(5)	6211.5(3)
Z	2	2	4	4	4	4	2	3
Formula weight	576.40	840.10	882.77	1246.91	1388.88	1558.76	1173.33	2029.49
Space group	$P\overline{1}$	$P\overline{1}$	C2/c	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P\overline{1}$	$P\overline{1}$
\tilde{T}/K	100(2)	110(2)	100(2)	100(2)	100(2)	100(2)	100(2)	173(2)
λ/Å	0.71073	0.71073	0.71073	1.54184	1.54184	1.54184	1.54184	0.71073
$D_{\rm c}/{\rm g~cm^{-3}}$	1.570	2.230	1.563	1.507	1.302	1.278	1.528	1.628
$\mu/\text{mm}-1$	0.950	9.246	1.120	8.070	2.958	2.333	7.827	1.382
Reflections	36726	48699	64425	90022	84768	93253	27607	196062
collected								
Independent	6041	7185	4458	11424	14703	16852	9682	25393
reflections								
	$R_{\rm int} = 0.0596$	$R_{\rm int} = 0.0418$	$R_{\rm int} = 0.0637$	$R_{\rm int} = 0.0279$	$R_{\rm int} = 0.0352$	$R_{\rm int} = 0.0925$	$R_{\rm int} = 0.0593$	$R_{\rm int} = 0.0513$
Goodness of fit	0.924	0.824	0.785	1.045	1.088	0.886	1.027	0.892
on F^2								
R(Fo),	0.0257	0.0166	0.0227	0.0236	0.0306	0.0397	0.0570	0.0314
$[I > 2\sigma(I)]$								
$R_{\rm w}(Fo^2)$	0.0613	0.0236	0.0429	0.0601	0.0846	0.0894	0.1557	0.0702
$\Delta \rho / e \text{ Å}^{-3}$	0.367/-0.298	0.626/-0.622	0.609/-0.416	0.377/-0.673	0.503/-0.685	0.504/-0.957	1.712/-0.892	1.423/-1.313

 ${}^{3}J({}^{13}C-{}^{11}B) = 2.7$ Hz, *m-Ph-B*), 130.2 (pst, ${}^{3}J_{CP} + {}^{5}J_{CP'}| = 5.0$ Hz, *m-Ph-P*), 132.1 (s, *p-Ph-P*), 132.2 (pst, ${}^{1}J_{CP} + {}^{3}J_{CP'}| = 22.5$ Hz, *ipso-Ph-P*), 134.4 (pst, ${}^{2}J_{CP} + {}^{4}J_{CP'}| = 5.6$ Hz, *o-Ph-P*), 136.8 (m, ${}^{2}J({}^{13}C-{}^{11}B) = 1.3$ Hz, *o-Ph-B*), 164.9 (m, ${}^{1}J({}^{13}C-{}^{11}B) = 50$ Hz, ${}^{1}J({}^{13}C-{}^{10}B) = 16.7$ Hz, *ipso-Ph-B*), 210.7 (t, ${}^{2}J_{CP} = 8.4$ Hz, Ru=*C*) ppm. ${}^{31}P{}^{1}H{}$ NMR (81.1 MHz, CD₃CN, 300 K): $\delta = +35.8$ ppm. Anal. calc'd for [5](BPh₄)₂·CHCl₃, C₁₀₁H₉₇B₂Cl₃N₄P₂Ru (1657.91): C 73.17, H 5.90, N 3.38; found: C 72.82, H 5.97, N 3.39.

Synthesis and characterization of 6

Solid [(MeCN)₂PdCl₂] (142 mg, 0.545 mmol, 1.54 equiv.) was added to a stirred solution of [4]Cl·THF (342 mg, 0.356 mmol) in CH₂Cl₂ (13 mL), which soon led to precipitation of bright yellow [PdCl₂(PPh₃)₂]. The reaction mixture was stirred for an additional hour and then, to complete the precipitation, stirred at 0 °C for 30 min. The precipitate was removed by filtration, and the filtrate was concentrated in vacuo to ca. 2 mL, and MeCN (10 mL) was added. Storing this solution at -30 °C for two days resulted in the crystallization of an orange microcrystalline solid. This was separated by filtration, washed with cold MeCN (2×2 mL) and dried in vacuo. Yield: 70% (231 mg). Single crystals suitable for Xray diffraction analysis were obtained by storing a concentrated MeCN solution at 5 °C. ¹H NMR (400.1 MHz, CD_2Cl_2): δ = 1.25–1.85 (m, 12H, β -/ γ -CH₂), 1.97 (s, 12H, free MeCN), 2.37 (s, 3H, coord. MeCN), 2.68 (d, ${}^{2}J_{HH}$ = 13 Hz, HC(H)N), 3.23 (m, 3H, CH_2), 3.88 (d, J = 12 Hz, CH_2), 4.03 (t, $J_{HH} = 12$ Hz, CH_2), 4.23 (d, $J_{\rm HH} = 12$ Hz, CH_2), 5.71 (d, ${}^{2}J_{\rm HH} = 13$ Hz, HC(H)N), 7.31–7.47 (m, 10H, *m*-/*p*-*Ph*P), 7.56–7.66 (m, 6H, *o*-*Ph*P) ppm. ³¹P{¹H} NMR (81.1 MHz, CD₂Cl₂): $\delta = +49.5$ ppm. Anal. calc'd for 6×3 MeCN, C₃₆H₄₄Cl₄N₅PPdRu (927.06): C 46.64, H 4.78, N 7.55; found: C 47.19, H 4.87, N 7.95.

Isolation of 7

Red–orange crystals of the solvate 7.4CH₂Cl₂ were obtained by storing a concentrated CH₂Cl₂ solution of **6** at ambient temperature for two days. The crystalline material was carefully dried *in vacuo* and used for combustion analysis. Single crystals suitable for X-ray diffraction analysis were obtained upon storing a concentrated CH₂Cl₂ solution at 5 °C. Because of the very low solubility of **7** in deuterated organic solvents, we were unable to collect sufficient NMR spectroscopic data. Anal. calc'd for 7×4CH₂Cl₂, C₆₄H₇₆Cl₈N₆P₂Pd₂Ru₂ (1689.91): C 45.49, H 4.53, N 4.97; found: C 45.32, H 4.37, N 5.32.

Single-crystal X-ray structure determination

Crystals were mounted on glass fibres in perfluorinated oil. Diffraction data for complexes 2a, 2b, 3 and 7 were collected with an Oxford Diffraction Xcalibur diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å) and for complexes [4]Cl, [4]BPh₄, $[5](BPh_4)_2$ and 6 with an Oxford Diffraction Nova diffractometer using Cu-K α radiation ($\lambda = 1.54184$ Å). The structures were solved with SHELXS-97³⁶ by direct methods and refined on F^2 with SHELX-97.37 Hydrogen atoms were included using rigid idealised methyl groups or a riding model. ORTEP-III for Windows³⁸ was used for all molecular plots. Special features and problems: Crystals of compound 3 diffracted weakly. Several structures were negatively affected by the presence of substantial amounts of incorporated solvent. For structures $[4]BPh_4$ and 6, the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands) was used to remove the effects of severely disordered solvent. Acetonitrile hydrogens proved difficult to locate, and their slow convergence indicated probable rotational disorder. In some cases, these H atoms were excluded from the refinement (for details,

see the ESI[†]). For structure **5**, two rings of the anion displayed alternative orientations; only one was consistent with the solvent site and was therefore assigned the same occupation factor as the solvent.

CCDC 819865–819872 (in the same order as Table 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Theoretical calculations

The calculations were performed using the *GAUSSIAN09* package.³⁹ All structures were fully optimized on the density functional theory (DFT) level employing the B3LYP,^{40,41} BP86,^{40,42} and M06-L hybrid functional.⁴³ For all main-group elements (C, H, N, P and Cl) the all-electron double- ζ basis set (6-31+G**) was used, whereas for the ruthenium atom a small-core relativistic ECP together with the corresponding double- ζ valence basis set was employed (Stuttgart RSC 1997 ECP).⁴⁴

Notes and references

- (a) R. N. Vrtis and S. J. Lippard, *Isr. J. Chem.*, 1990, **30**, 331–341;
 (b) E. M. Carnahan, J. D. Protasiewicz and S. J. Lippard, *Acc. Chem. Res.*, 1993, **26**, 90–97;
 (c) A. J. L. Pombeiro, M. F. C. Guedes da Silva and R. A. Michelin, *Coord. Chem. Rev.*, 2001, **218**, 43–74.
- 2 For reductive coupling of coordinated isocyanides, see: (a) C. T. Lam, P. W. R. Corfeld and S. J. Lippard, J. Am. Chem. Soc., 1977, 99, 617– 618; (b) J. C. Dewan, C. M. Giandomenico and S. J. Lippard, Inorg. Chem., 1981, 20, 4069–4074; (c) C. M. Giandomenico, C. T. Lam and S. J. Lippard, J. Am. Chem. Soc., 1982, 104, 1263–1271; (d) S. Warner and S. J. Lippard, Organometallics, 1986, 5, 1716–1725; (e) J. A. Acho and S. J. Lippard, Organometallics, 1994, 13, 1294–1299; (f) C. Collazo, D. Rodewald, H. Schmidt and D. Rehder, Organometallics, 1996, 15, 4884–4887; (g) M. H. Chisholm, D. Ho, J. C. Huffman and N. S. Marchant, Organometallics, 1989, 8, 1626–1636.
- 3 For electrophile induced coupling of isocyanides and/or aminocarbyne ligands, see: (a) A. C. Filippou, W. Grünleitner, C. Völkl and P. Kiprof, Angew. Chem., 1991, 103, 1188–1191, (Angew. Chem., Int. Ed. Engl., 1991, 30, 1167–1169); (b) A. C. Filippou and W. Grünleitner, Z. Naturforsch., 1989, B44, 1023–1034; (c) A. C. Filippou and W. Grünleitner, Z. Naturforsch., 1991, B46, 216–230; (d) A. C. Filippou, Polyhedron, 1990, 9, 727–736; (e) A. C. Filippou, B. Lungwitz and G. Kociok-Köhn, Eur. J. Inorg. Chem., 1999, 1905–1910; (f) A. C. Filippou, C. Völkl, W. Grünleitner and P. Kiprof, J. Organomet. Chem., 1992, 434, 201–223.
- 4 For proton-induced aminocarbyne coupling reactions, see: (a) J. J. R. Fraústo da Silva, M. A. Pellinghelli, A. J. L. Pombeiro, R. L. Richards, A. Tiripicchio and Y. Wang, J. Organomet. Chem., 1993, 454, C8–C10; (b) Y. Wang, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, M. A. Pellinghelli, A. Tiripicchio, R. A. Henderson and R. L. Richards, J. Chem. Soc., Dalton Trans., 1995, 1183–1191; (c) R. A. Henderson, A. J. L. Pombeiro, R. L. Richards, J. J. R. Fraústo da Silva and Y. Wang, J. Chem. Soc., Dalton Trans., 1995, 1193–1199.
- 5 (a) E. O. Fischer, D. Wittmann, D. Himmelreich and D. Neugebauer, Angew. Chem., 1982, 94, 451–452, (Angew. Chem., Int. Ed. Engl., 1982, 21, 444), see also: (b) E. O. Fischer and R. Reitmeier, Z. Naturforsch., 1983, 38b, 582–586.
- 6 A. C. Filippou and T. Rosenauer, *Angew. Chem.*, 2002, **114**, 2499–2502, (*Angew. Chem., Int. Ed.*, 2002, **41**, 2393).
- 7 (a) J. Heck, K.-A. Kriebisch, W. Massa and S. Wocaldo, J. Organomet. Chem., 1994, 482, 81–84; (b) W. Abriel, G. Baum, J. Heck and K.-A. Kriebisch, Chem. Ber., 1990, 123, 1767–1778.
- 8 C. Hartbaum, E. Mauz, G. Roth, K. Weissenbach and H. Fischer, Organometallics, 1999, 18, 2619–2627.
- 9 Several protocols are known that usually require the stepwise addition of amines/amides to *in situ* prepared dihaloacetylenes or chloroaminoacetylenes: (a) S. Y. Deluvarenne and H. G. Viehe, *Chem. Ber.*, 1970, **103**, 1198–1208; (b) L. Réne, Z. Janousek and H. G. Viehe, *Synthesis*, 1982, **8**, 645; (c) L. Brandsma and H. D. Verkruijsse, *Synth.*

Commun., 1991, **21**, 811–813; (d) G. Himbert, H. Naßhan and S. Kosack, Synlett, 1991, 117–118.

- 10 H. G. Viehe and M. Reinstein, Angew. Chem., 1964, 76, 537, (Angew. Chem., Int. Ed. Engl., 1964, 3, 506).
- (a) D. Holschumacher, C. G. Hrib, P. G. Jones and M. Tamm, *Chem. Commun.*, 2007, 3661–3663; (b) H. Schumann, M. Glanz, F. Girgsdies, F. E. Hahn, M. Tamm and A. Grzegorzewski, *Angew. Chem.*, 1997, 109, 2328–2330, (*Angew. Chem., Int. Ed. Engl.*, 1997, 36, 2232–2234).
- 12 A. R. Petrov, C. G. Daniliuc, P. G. Jones and M. Tamm, *Chem.-Eur. J.*, 2010, **16**, 11804–11808.
- 13 Highlighted in: T. M. Swager and S. Liu, Synfacts, 2010, 12, 1368.
- 14 F. W. Grevels and V. Skibbe, J. Chem. Soc., Chem. Commun., 1984, 681–683.
- 15 J. A. Connor, E. M. Jones, E. W. Randall and E. Rosenberg, J. Chem. Soc., Dalton Trans., 1972, 2419–2424.
- 16 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, J. Chem. Soc., Perkin Trans. 2, 1987, S1–S19.
- 17 M. A. Bennett, T. N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, 21, 74–78.
- 18 (a) W. A. Herrmann, C. Köcher, L. J. Gooßen and G. R. J. Artus, *Chem.-Eur. J.*, 1996, 2, 1627–1636; (b) P. Csabai and F. Joó, *Organometallics*, 2004, 23, 5640–5643; (c) M.-E. Moret, A. B. Chaplin, A. K. Lawrence, R. Scopelliti and P. J. Dyson, *Organometallics*, 2005, 24, 4039–4048; (d) C. Lo, R. Cariou, C. Fischmeister and P. H. Dixneuf, *Adv. Synth. Catal.*, 2007, 349, 546–550; (e) L. Mercs, A. Neels and M. Albrecht, *Dalton Trans.*, 2008, 5570–5576; (f) X.-Q. Xiao and G.-X. Jin, *Dalton Trans.*, 2009, 9298–9303.
- 19 (a) E. Solari, S. Gauthier, R. Scopelliti and K. Severin, Organometallics, 2009, 28, 4519–4526 and references therein; (b) R. Goerissen, U. Koelle and T. Spaniol, Polyhedron, 1992, 11, 2317–2320.
- 20 (a) B. M. Trost and A. McClory, *Chem.-Asian J.*, 2008, **3**, 164–194;
 (b) B. M. Trost, M. U. Frederiksen and M. T. Rudd, *Angew. Chem.*, 2005, **117**, 6788–6825, (*Angew. Chem., Int. Ed.*, 2005, **44**, 6630); (c) B. M. Trost, *Acc. Chem. Res.*, 2002, **35**, 695–705; (d) B. M. Trost, F. D. Toste and A. B. Pinkerton, *Chem. Rev.*, 2001, **101**, 2067–2096.
- 21 (a) M. I. Bruce, Coord. Chem. Rev., 2004, 248, 1603–1625; (b) M. I. Bruce, Chem. Rev., 1998, 98, 2797–2858; (c) M. I. Bruce, Chem. Rev., 1991, 91, 197–257.
- (a) B. Dutta, B. F. E. Curchod, P. Campomanes, E. Solari, R. Scopelliti,
 U. Rothlisberger and K. Severin, *Chem.-Eur. J.*, 2010, 16, 8400–8409;
 (b) J. M. Lynam, *Chem.-Eur. J.*, 2010, 16, 8238–8247.
- 23 (a) T. A. Stephenson and G. Wilkinson, J. Inorg. Nucl. Chem., 1966, 28, 945–956; (b) S. D. Robinson and G. Wilkinson, J. Chem. Soc. A, 1966, 300–301; D. J. Cole-Hamilton and G. Wilkinson, J. Chem. Soc., Dalton Trans., 1979, 1283–1289.
- 24 (a) P. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, Angew. Chem., 1995, **107**, 2179–2181, (Angew. Chem., Int. Ed. Engl., 1995, **34**, 2039–2041); (b) E. A. Shaffer, C.-L. Chen, A. M. Beatty, E. J. Valente and H.-J. Schanz, J. Organomet. Chem., 2007, **692**, 5221–5233.
- 25 J. L. Templeton, Adv. Organomet. Chem., 1989, **29**, 1–100.
- 26 S. Alvarez and J. Cirera, Angew. Chem., 2006, 118, 3078–3087, (Angew. Chem., Int. Ed., 2006, 45, 3012–3020).
- 27 B. Askevold, M. M. Khusniyarov, E. Herdtweck, K. Meyer and S. Schneider, *Angew. Chem.*, 2010, **122**, 7728–7731, (*Angew. Chem., Int. Ed.*, 2010, **49**, 7566–7569).
- 28 (a) L. A. Watson, O. V. Ozerov, M. Pink and K. G. Caulton, J. Am. Chem. Soc., 2003, **125**, 8426–8427; (b) A. Walstrom, M. Pink, N. P. Tsvetkov, H. Fan, M. Ingleson and K. G. Caulton, J. Am. Chem. Soc., 2005, **127**, 16780–16781; (c) X. Yang, A. Walstrom, N. Tsvetkov, M. Pink and K. G. Caulton, Inorg. Chem., 2007, **46**, 4612–4616.
- 29 K. Tatsumi, R. Hoffmann and J. L. Templeton, *Inorg. Chem.*, 1982, 21, 466–468.
- 30 S. O. Grim and R. L. Keiter, Inorg. Chim. Acta, 1970, 4, 56-60.
- 31 See for instance: A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer and O. R. Thiel, *Chem.-Eur. J.*, 2001, 7, 3236-3253; C. S. Diesendruck, E. Tzur, A. Ben-Asuly, I. Goldberg, B. F. Straub and N. G. Lemcoff, *Inorg. Chem.*, 2009, 48, 10819-10825; I. Karame, M. Boualleg, J.-M. Camus, T. K. Maishal, J. Alauzun, J.-M. Basset, C. Copéret, R. J. P. Corriu, R. Jeanneau, A. Mehdi, C. Reyé, L. Veyre and C. Thieuleux, *Chem.-Eur. J.*, 2009, 15, 11820-11823; F. Grisi, A. Mariconda, C. Costabile, V. Bertolasi and P. Longo, *Organometallics*, 2009, 28, 4988-4995; I. Özdemir, S. Demir, N. Gürbüz, B. Çetinkaya, L. Toupet, C. Bruneau and P. H. Dixneuf, *Eur. J. Inorg. Chem.*, 2009, 1942–1949; A. A. Danopoulos, S. Winston and W. B. Motherwell, *Chem. Commun.*, 2002, 1376–1377.

- 32 See for instance: J. Schütz, E. Herdtweck and W. A. Herrmann, Organometallics, 2004, 23, 6084–6086; A. Fürstner, G. Seidel, D. Kremzow and C. W. Lehmann, Organometallics, 2003, 22, 907–909; R. A. Michelin, M. Mozzon, M. Zecca, B. Corain, O. Piazzi and G. Zanotti, Inorg. Chim. Acta, 1990, 174, 3–7; S.-T. Liu, T.-Y. Hsieh, G.-H. Lee and S.-M. Peng, Organometallics, 1998, 17, 993–995; J. A. Chamizo, J. Morgado, M. Castro and S. Bernès, Organometallics, 2002, 21, 5428– 5432.
- 33 M. Melaimi, M. Soleilhavoup and G. Bertrand, Angew. Chem., 2010, 122, 8992–9032, (Angew. Chem., Int. Ed., 2010, 49, 8810– 8849).
- 34 W. Strohmeier and K. Gerlach, Chem. Ber., 1961, 94, 398-406.
- 35 (a) M. Noskowska, E. Sliwinska and W. Duczmal, *Transition Met. Chem.*, 2003, 28, 756–759; (b) M. A. Andrews, T. C.-T. Chang, C.-W. F. Cheng, L. V. Kapustay, K. P. Kelly and M. J. Zweifel, *Organometallics*, 1984, 3, 1479–1484.
- 36 G. M. Sheldrick, SHELXS-97, Acta Crystallogr., Sect. A: Found. Crystallogr., 1990, 46, 467–473.
- 37 G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112–122.
- 38 L. J. Farrugia, ORTEP-3, University of Glasgow, Scotland, 1999.
- 39 Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
- 40 (a) A. D. Becke, Phys. Rev. A, 1988, 38, 3098–3100; (b) A. D. Becke, J. Chem. Phys., 1993, 98, 5648–5652.
- 41 C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785-789.
- 42 J. P. Perdew, Phys. Rev. B, 1986, 33, 8822-8824.
- 43 Y. Zhao and D. G. Truhlar, J. Chem. Phys., 2006, 125, 194101.
- 44 M. Dolg, H. Stoll, H. Preuss and R. M. Pitzer, J. Phys. Chem., 1993, 97, 5852–5859.