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Reactivity of a binuclear Ru(II) N_2-bridged complex towards phosphines: facile access to novel mono and binuclear phosphorous derivatives. X-ray structural characterization of two unusual binuclear complexes containing 'pincer' ligands: $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}\eta^2\text{-}P_2)]$ (NN′N = 2,6-bis[(dimethylamino)methyl]pyridine; P_2 = 1,3-bis[(diphenylphosphino)methyl]benzene or 1,3-bis(diphenylphosphino)propane)☆

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Abstract

Treatment of the dinitrogen bridged complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ (**1**, NN′N = 2,6-bis[(dimethylamino)methyl]pyridine) with a variety of monodentate phosphorous ligands results in the formation of the corresponding mononuclear derivatives $[RuCl_2(\eta^3\text{-}NN'N)(PR_3)]$ ($R_3 = Ph_3$, **2**; Ph_2H, **3**; Me_3, **4**; $(OMe)_3$, **5**). When potentially bidentate bis-phosphines are used, the results are found to be ligand dependent: with one or two equivalents of bis(diphenylphosphino)methane (dppm), the only product observed is the mononuclear derivative $[RuCl_2(\eta^2\text{-}NN'N)(\eta^2\text{-dppm})]$ (**6**), which contains the diphosphine acting as a chelating ligand. However, the use of bis-phosphines such as 1,2-bis(diphenylphosphino)ethane (dppe), 1,3-bis(diphenylphosphino)propane (dppp) or 1,1′-bis[di(*p*-tolyl)phosphino]ferrocene (dtpf), results in the formation of binuclear products: $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-dppe})]$ (**7**), $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-dppp})]$ (**8**) and $[(RuCl_2(\eta^3\text{-}NN'N))_2(\mu\text{-dtpf})]$ (**9**), respectively. In these cases, the phosphine ligands are bridging between two Ru centered moieties. The X-ray structure of complex **8** is reported. Treatment of complex **1** with the potentially terdentate phosphine ligand 1,3-bis[(diphenylphosphino)methyl]benzene (PCHP) affords the binuclear derivative $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}\eta^2\text{-PCHP})]$ (**10**). Compound **10** has been characterized by X-ray diffraction methods and represents the first example in which a Ru complex contains a bridging and noncyclometallated PCHP 'pincer' ligand. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium complexes; Bridging bis-phosphines; Binuclear compounds; Pincer complexes; Cyclometallation intermediates

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☆ Dedicated to Professor Alberto Ceccon on the occasion of his 65th birthday.

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1. Introduction

Mononuclear Ru(II) complexes containing the terdentate 'pincer' ligand 2,6-bis[(dimethylamino)-methyl]pyridine (NN′N) show high catalytic activity in the cycloalkylation of aromatic amines with alcohols to give piperazines and piperidines [1]. For example, the compound $[RuCl_2(\eta^3\text{-}NN'N)(PPh_3)]$ (**2**) [2], or its cationic derivatives, showed greatly enhanced catalytic activity for this cyclization reaction when compared to some classical ruthenium precursors such as $[RuCl_2(PPh_3)_3]$ [1,3].

It is well known that the nature of the phosphine ligands attached to a catalyst precursor has an important influence on the versatility of the resulting active system. By varying the substituent groups on the phosphorous atoms (R of PR_3), one can influence the activity, selectivity and stability of a catalytic process via ligand electronic and/or steric properties [4]. In this context, attempts to increase the catalytic activity demonstrated by **2** have been carried out by the substitution of the triphenylphosphine ligand. Unfortunately, the direct treatment of **2** with basic phosphines (e.g. PMe_3), results in the formation of $[RuCl_2(PR_3)_4]$ compounds. These products arise from the replacement of the triphenylphosphine and the NN′N ligand by the incoming phosphine.

Recently, we have observed the high reactivity of the related dinitrogen bridged binuclear complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ (**1**) towards alkenes, alkynes and sulfur derivatives [2,5]. The ease at which these ligands can break the dinitrogen bridge to yield the corresponding mononuclear derivatives prompted us to study the reactivity of **1** towards monodentate phosphines in an attempt to devise a high yield synthetic protocol for complexes of general formula $[RuCl_2(\eta^3\text{-}NN'N)(PR_3)]$.

In addition to these studies, we described the reactivity of complex **1** towards potentially bi or terdentate phosphine ligands. In the course of this study, we succeeded in isolating a binuclear complex which contains the 'pincer' ligand 1,3-bis[(diphenylphosphino)methyl]benzene (PCHP) bridging between two Ru centered moieties. This represents the first example of this ligand co-ordination mode for this 'pincer' ligand in the chemistry of ruthenium, although it had been previously proposed as an intermediate in the formation of the organometallic complex $[Ru(\eta^3\text{-}PCP)(\eta^2\text{-}PCHP)][OTf]$ (OTf = trifluoromethyl sulfonate) [6]. This latter species has been hypothesized to be an important intermediate in the cyclometallation of aromatic compounds of the general formula $[1,3\text{-}(ER_nCH_2)_2C_6H_4]$ (E = P, S, N; $n = 1, 2$; i.e. the 'pincer' class of ligands) [7]. A large number of complexes containing the orthometallated monoanionic ligand $[PCP]^-$ and its diaminoaryl analog $[NCN]^-$ have been shown to be effective catalysts in a wide range of organic transformations (i.e. hydrogenation, isomerization, alkylation, etc.) [7c,8]. The characterization of these intermediate species will help to shed some light on the pathway of orthometallation in this important class of organometallic complexes [7b].

2. Results and discussion

Treatment of compound $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ (**1**, Fig. 1) with excess of triphenylphosphine in CH_2Cl_2 at room temperature (r.t.) affords, in good yields, the previously reported mononuclear derivative $[RuCl_2(\eta^3\text{-}NN'N)(PPh_3)]$ (**2**, Fig. 1) [2]. Compound **2** had been characterized by X-ray diffraction methods and presents an octahedral geometry about Ru with the terdentate NN′N and the phosphine ligands in the equatorial plane, a situation which forces the two chlorine atoms to be *trans*-positioned with respect to one another [2]. The synthetic route previously used for the synthesis of **2** implies treatment of the penta-coordinate complex $[RuCl_2(PPh_3)_3]$ [9] with one equivalent of the NN′N ligand in CH_2Cl_2 at r.t., to afford **2** (96% yield). However, this procedure could not be extended to other Ru complexes containing phosphines more basic than PPh_3, since the pyridine ligand is unable to displace these donors from the metal center. Moreover, treatment of complex **2** with one or more equivalent of phosphines such as PMe_3 or P^nBu_3 results in the formation of mixtures of products, in which the presence of $[RuCl_2(PR_3)_4]$ (R = Me or ^{n}Bu) could be detected. The procedure described above for the synthesis of **2** from **1**, offers one possible route to a new series of complexes containing other phosphine ligands.

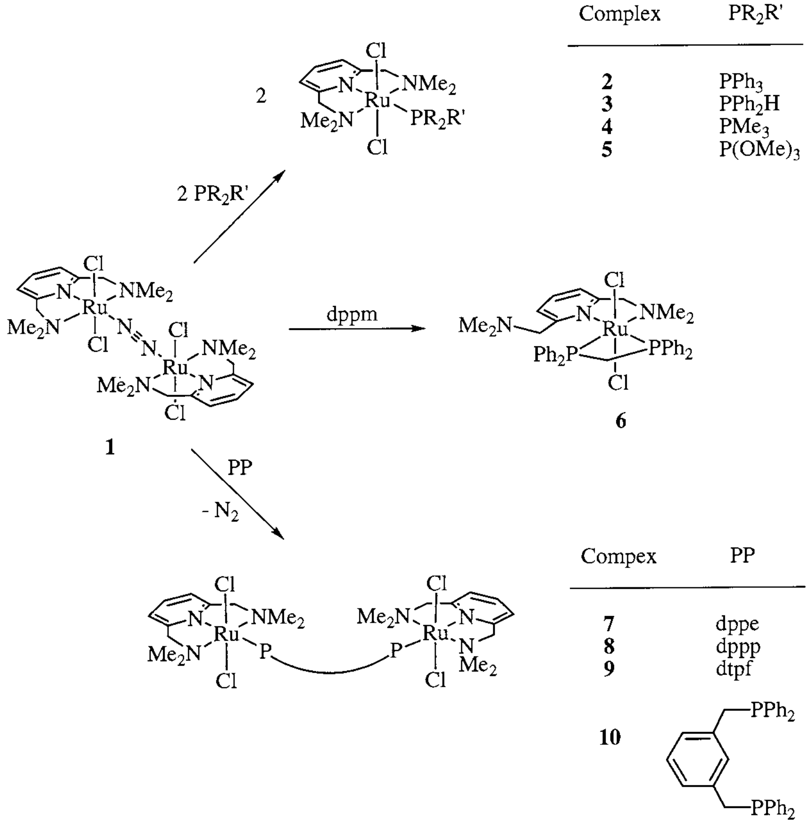
Treatment of complex **1** with two equivalents of diphenylphosphine results in the formation of the monosubstituted derivative $[RuCl_2(\eta^3\text{-}NN'N)(PPh_2H)]$ (**3**, Fig. 1) in 86% isolated yield. The ^1H-NMR spectrum of complex **3** (Table 1) shows singlets for the methyl groups and for the CH_2 protons of the pyridine ligand, which appear at $\delta = 2.02$ and 4.00, respectively, suggesting a similar ligand arrangement to that observed in **2**. The hydrogen atom attached to phosphorous appears as a doublet in the ^1H-NMR spectrum at $\delta = 7.85$ ($J_{H-P} = 340$ Hz), which is in the expected range for similar complexes containing the diphenylphosphine ligand [10]. The structure proposed for complex **3** (Fig. 1) is corroborated by its $^{31}P\{^1H\}$-NMR spectrum, which shows a singlet resonance ($\delta_P = 41.1$ ppm). This chemical shift value is similar to that observed for **2** and unequivocally indicates the co-ordination of the phosphine ligand [11]. The thermal activation of a P–H bond of a diphenylphosphine ligand is a common method to obtain metal–phosphido derivatives via HCl elimination [12]. However, heating of complex **3** in 1,2-dichloroethane at reflux temperature (86°C) for extended periods does not result in any spectral changes. This demonstrates a high thermal stability for **3**, a property that is necessary for applications in high temperature catalysis, such as our cycloalkylation reactions [1].

In previous work, we reported that treatment of the analogous Pt(II)-diphenylphosphine complex [Pt(NCN)($PHPh_2$)]X (NCN = 1,3-bis[(dimethylamino)methyl]benzene, X = [BF_4], [OSO_2CF_3]) with one equivalent of ^{n}BuLi, affords the corresponding neutral, mononuclear, terminal phosphido complex [Pt(NCN)(PPh_2)] [10b]. However, similar treatment of complex **3** with one or more equivalent of ^{n}BuLi leads to the formation of mixtures of products which probably arise from the attack at the chlorine atoms of the fragment containing the metal center, since the presence of the hydrogen atom attached to phosphorous could be still observed (^{1}H-NMR). The use of an alternative base such as LDA also leads to mixtures of many complexes, probably due to the instability of the intermediate products which are formed.

Treatment of **1** with two equivalents of trimethylphosphine at r.t. affords, as the only detected product, the corresponding mononuclear derivative [$RuCl_2(\eta^3$-NN′N)(PMe_3)] (**4**, Fig. 1). No other products arising from the dissociation of the pyridine ligand could be observed. The ^{1}H-NMR spectrum of **4** contains resonances which are assigned to the methyl and to the CH_2 protons of the NN′N ligand (singlets at $\delta = 2.45$ and 4.02, respectively). This results suggest idealized C_{2v} geometry for **4**, as observed in **2** and **3**. The $^{31}P\{^1H\}$-NMR spectrum of **4** presents one singlet at 2.5 ppm, in the expected region for a trimethylphosphine ligand co-ordinated to Ru [13].

A similar compound to those described above could be obtained when a tertiary phosphite is used as a reactant instead of a phosphine. Thus, treatment of **1** with two equivalents of trimethylphosphite in CH_2Cl_2 at r.t. affords the mononuclear derivative [$RuCl_2(\eta^3$-NN′N)(P{OMe}$_3$)] (**5**, Fig. 1) in 85% yield. The ^{1}H and $^{31}P\{^1H\}$ spectra of this complex confirm that the structure of **5** is analogous to that of **2**–**4** above (Table 1) [14].

The mild reaction conditions used in the formation of **2**–**5**, prompted us to study the reactivity of **1** towards potentially bidentate bis-phosphines. Many ruthenium complexes containing bidentate phosphine ligands are known, and some are excellent catalysts in a wide variety of organic transformations [14b]. The stability of chelate products has been surmised as an important reason for the high catalytic activity and



Complex	PR_2R'
2	PPh_3
3	PPh_2H
4	PMe_3
5	$P(OMe)_3$

Compex	PP
7	dppe
8	dppp
9	dtpf

Fig. 1. dppm, 1,1′-bis(diphenylphosphino)methane; dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis(diphenylphosphino)propane; dtpf, 1,1′-bis[di(*p*-tolyl)phosphino]ferrocene.

Table 1
Selected ^{1}H- and ^{31}P{^{1}H}-NMR data of compounds **2**–**10** [a,b,c,d,e,t]

Compound	NN′N ligand				Phosphine ligands	
	H_1	H_2	$C\mathit{H}_2$	$N\mathit{Me}_2$	Protons	*P*
2	7.65(t, 7.8)	–	4.00	2.10	–	37.0
3	7.72(t, 7.8)	7.36(d, 7.8)	4.00	2.02	7.85(d, 340)[f]	41.1
4	7.70(t, 7.8)	7.37(d, 7.8)	3.91	2.28	1.62(d, 7.3)[g]	2.5
5	7.75(t, 7.8)	7.36(d, 7.8)	4.02	2.45	3.95[h]	144.8
6	–	–	4.49, 3.78	2.55, 1.80	4.85(t, 10.6)[i]	12.2(d, 68.6) 4.0(d, 68.6)
7	7.87(t, 7.8)	7.57(d, 7.8)	3.86	1.90	2.64(dd, 49.5 and 12.4)[j]	37.1
8	7.67(t, 7.8)	7.31(d, 7.8)	3.91	1.89	3.20(m)[k], 2.30(m)[l]	24.4
9	7.66(t, 7.8)	7.29(d, 7.8)	3.87	1.80	2.41[m], 3.34(br)[n], 3.57(br)[o]	29.6
10	7.81(t, 7.8)	7.45(d, 7.8)	4.00	2.05	4.02[p], 5.93(m)[q], 6.40(m)[r], 6.49(m)[s]	39.5

[a] Spectra recorded using CD_2Cl_2 as solvent.
[b] All signals are singlets unless otherwise stated.
[c] Key: d, doublet; t, triplet; m, multiplet; br, broad.
[d] Coupling constants (parentheses) in Hertz.
[e] All spectra reported correct integration for the proposed structures.
[f] $P\mathit{H}Ph_2$.
[g] $P(C\mathit{H}_3)_3$.
[h] $P(OC\mathit{H}_3)_3$.
[i] $C\mathit{H}_2$.
[j] $C\mathit{H}_2$.
[k] $C\mathit{H}_2CH_2C_{H_2}$.
[l] $CH_2C\mathit{H}_2CH_2$.
[m] $P[\mathit{p}\text{-}(C_6H_4C\mathit{H}_3)_2]$.
[n] *o*-C*H*, Cp ring.
[o] *m*-C*H*, Cp ring.
[p] $C\mathit{H}_2$.
[q] *o*-C*H* respect to both phosphorous.
[r] *o*-C*H*.
[s] *p*-C*H*.
[t] All the signals corresponding to the phenyl rings have been omitted for simplicity.

robust nature of this type of complex. Moreover, other such compounds have been postulated as primary catalytic intermediates [14b].

When complex **1** is treated with one equivalent of bis(diphenylphosphino)methane (dppm) in CH_2Cl_2 (r.t.), the ^{1}H- and ^{31}P{^{1}H}-NMR data of the resulting reaction mixture indicate the formation of the new mononuclear derivative [$RuCl_2$(η^2-NN′N)(η^2-dppm)] (**6**, Fig. 1), while half of the starting material remains unreacted. No traces of a binuclear compound, such as [{$RuCl_2$(η^3-NN′N)}$_2$(μ-dppm)], have been observed even after extended reaction times. Treatment of the reaction mixture with another equivalent of dppm affords exclusively compound **6** (64% yield). Complex **6** contains a Ru atom in an octahedral geometry with both bidentate ligands placed in the equatorial plane, while the chlorine atoms occupy apical positions *trans*-positioned to each other. The η^2-co-ordination mode for the pyridine ligand in **6** is clearly reflected by its ^{1}H-NMR spectrum, which shows one singlet for each of the two inequivalent NMe_2 groups ($\delta = 2.55$ and 1.80, respectively), while the resonances corresponding to the CH_2 groups appear also as singlets ($\delta = 4.49$ and 3.78 ppm). The structure proposed for **6** (Fig. 1) is also confirmed by its ^{31}P{^{1}H}-NMR data, which show the presence of two inequivalent phosphorous atoms ($\delta_P =$ 12.2 and 4.0, respectively, $J_{P-P} = 68.6$ Hz). These data permit us to discard any other ligand arrangement (i.e. chlorine atoms *cis*-positioned), since this would result in inequivalent resonances for the protons of the co-ordinated CH_2 group, as is observed for other complexes containing the NN′N ligand in a position without a C_2 axis or a mirror plane [2]. The NMR data of **6** also reflect the existence of a fluxional process involving one of the ‘arms’ of the NN′N ligand (^{1}H-NMR: $\delta = 1.80$ [NMe_2] and $\delta = 3.78$ [CH_2]) and one of the phosphine groups of dppm ($\delta_P = 4.0$ ppm). This is reflected by the broad appearance of the above mentioned resonances in the corresponding NMR spectra. This fluxionality can be arrested at low temperature (200 K). The low temperature structure for complex **6** is depicted in Fig. 1. However, the high temperature limit which may contain an η^3-co-ordination mode for the NN′N ligand, while the dppm is η^1-coordinated, could not be reached. Similar fluxional processes involving bidentate phosphorous ligands in other Ru complexes have been reported previously [15].

One of the reasons one can give to explain this fluxional process in **6**, is the existence of an energetically unfavorable four-member ring (Ru–P–C–P), together with the presence of a free donor (NMe_2) group of the pyridine ligand. Therefore, one would expect that the substitution of dppm for another bidentate phosphine ligand containing a longer carbon chain (e.g. 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(-diphenylphosphino)propane (dppp)), should result in the formation of more stable five- and six-member rings, respectively. However, separate treatment of **1** with two equivalents of these phosphines results in the formation of new binuclear complexes [{$RuCl_2$(η^3-NN′N)}$_2$(μ-dppe)] (**7**) and [{$RuCl_2$(η^3-NN′N)}$_2$(μ-dppp)] (**8**, Fig. 1), respectively, while the presence of free phosphine and some other minor compounds (less than 10%, $^{31}P\{^1H\}$- and ^1H-NMR integration), could be detected in the reaction mixture. The symmetry properties of complexes **7** and **8** are reflected in their corresponding ^1H- and $^{31}P\{^1H\}$-NMR spectra. The $^{31}P\{^1H\}$-NMR data show a singlet for the two equivalent phosphorous atoms at $\delta = 37.1$ for **7** and at 24.4 for **8**, while the ^1H-NMR data show the CH_2 and the NMe_2 groups of the pyridine ligand at $\delta = 3.86$ and 1.90, respectively, for **7** and at $\delta = 3.91$ and 1.89 for **8**. Further treatment of these complexes with another equivalent of the corresponding diphosphine at r.t. does not result in any spectral changes, apart from the observation of free phosphine ligand. Heating of this reaction mixture results in the formation of an untractable mixture of products.

The structure of **8** in solid state has been determined via a X-ray diffraction study on a single crystal of **8**. Crystal and refinement data are listed in Section 4. A molecular plot and selected bond distances and angles are given in Fig. 2. The structure confirms the data observed in solution, with **8** displaying a bridging dppp ligand between two Ru-centered moieties. Although this compound is symmetrical in solution, this symmetry is not preserved in the solid state. The bond distances are in the range of those observed for analogous complexes containing bridging dppp ligands [16].

Treatment of complex **1** with one equivalent of 1,1′-bis[di(*p*-tolyl)phosphino]ferrocene (dtpf) (CH_2Cl_2; r.t.) affords the mixed trinuclear complex [{$RuCl_2$(η^3-NN′N)}$_2$(μ-dtpf)] in good yields (**9**, Fig. 1). The molecular symmetry of complex **9** is reflected by its ^1H- and $^{31}P\{^1H\}$-NMR data (Table 1). These data unequivocally confirm the proposed bridging co-ordination mode of the phosphorous ligand [17]. The interest in binuclear and polynuclear complexes, particularly of

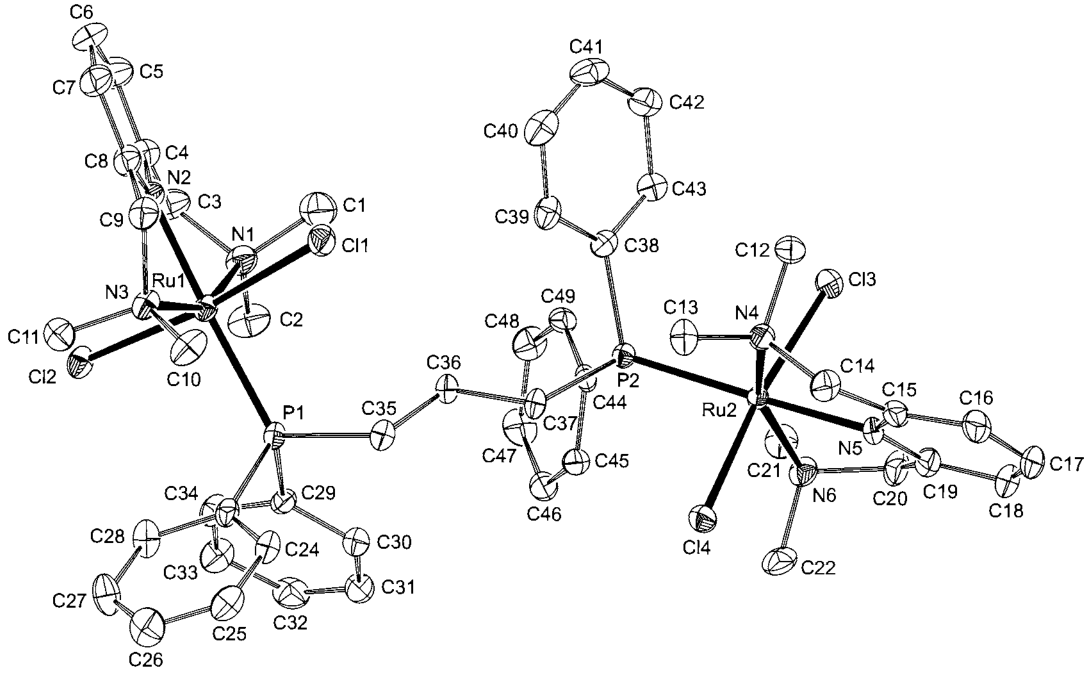


Fig. 2. Molecular structure of compound **8**. Displacement ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å), angles (°) and torsion angles (°): Ru(1)–Cl(1) 2.4286(13), Ru(1)–Cl(2) 2.4432(12), Ru(2)–Cl(3) 2.4502(13), Ru(2)–Cl(4) 2.4383(13), Ru(1)–N(1) 2.217(4), Ru(1)–N(2) 2.025(4), Ru(1)–N(3) 2.228(4), Ru(2)–N(4) 2.189(4), Ru(2)–N(5) 2.027(4), Ru(2)–N(6) 2.240(4), Ru(1)–P(1) 2.3391(13), Ru(2)–P(2) 2.3270(13); Cl(1)–Ru(1)–Cl(2) 173.17(4), Cl(3)–Ru(2)–Cl(4) 173.27(4), N(1)–Ru(1)–N(3) 156.27(14), N(4)–Ru(2)–N(6) 157.83(14), N(2)–Ru(1)–P(1) 177.33(11), N(5)–Ru(2)–P(2) 176.85(11), Ru(1)–P(1)–C(35) 116.62(17), Ru(2)–P(2)–C(37) 117.58(14), P(1)–C(35)–C(36) 117.0(3), P(2)–C(37)–C(36) 117.6(3), C(35)–C(36)–C(37) 110.4(4); N(1)–C(3)–C(4)–N(2) −34.7(6), N(2)–C(8)–C(9)–N(3) −26.0(6), N(4)–C(14)–C(15)–N(5) −33.0(6), N(5)–C(19)–C(20)–N(6) −23.8(6).

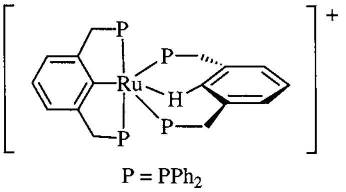


Fig. 3.

the Group 8 metals, has been brought about to a large degree by the anticipation that such complexes may display metal–metal co-operativity effects in substrate activation and catalysis [18]. Particularly, 1,1′-bis-(diphenylphosphino)ferrocene (dppf) and dtpf hetero-polymetallic species have attracted significant attention because of their interesting co-operative effects between metal sites, in addition to their catalytic potential [19].

In order to get some knowledge about the different behavior shown by the dppm ligand in complex **6** when compared with the other bidentate phosphines used in this work, molecular mechanic simulations based on the X-ray structure data of complex **8** were carried out at the MM2 calculation level. Although absolute values cannot be achieved with the MM2 basis set, qualitative data show that the energies of complexes which contain η^1-P-(mono)co-ordinated dppm or dppp ligands are in the same range ($\Delta E = 0.59$ kcal mol^{-1}). In contrast, complexes which contain these diphosphine ligands bonded in a η^2-P,P′-chelating mode, show a $\Delta E = E_{\mathrm{dppp}} - E_{\mathrm{dppm}} = 12.79$ kcal mol^{-1}. The relative energies are inverted when binuclear complexes containing bridging dppm or dppp are modeled, observing in this case a $\Delta E = E_{\mathrm{dppp}} - E_{\mathrm{dppm}} = -7.31$ kcal mol^{-1}. These relative differences in energy between the two possible co-ordination modes, i.e. bridging versus chelating, may be the possible reason for the fact that the dppm ligand in complex **6** is chelate bonded whereas in the other complexes described in this work the diphosphine ligand are bridging.

The ruthenium complex [RuCl(η^3-PCP)(PPh$_3$)], (PCP = 2,6-[$C_6H_3(CH_2PPh_2)_2]^-$) and its derivatives show high catalytic activity in hydrogen-transfer reactions [7c]. In a recent report, the synthesis and X-ray characterization of the mononuclear cationic complex [Ru(η^3-PCP)(η^2-PCHP)][OTf] (PCHP = [$C_6H_4(CH_2PPh_2)_2$-2,6]; OTf$^-$ = trifluoromethyl sulfonate) was described. This compound contains one monoanionic [PCP]$^-$ and one neutral PCHP ‘pincer’ fragment and can be regarded as an intermediate in the cyclometallation of a ‘pincer’ ligand (Fig. 3) [6]. The formation of this compound is thought to occur via a binuclear intermediate containing a bridging PCHP ligand. However, this intermediate could not be isolated, probably due to the high tendency of the PCHP ligand to form chelated and orthometallated species. This is due in part to the short P–P distance (4.60–4.90 Å), which can produce a strong interaction of the central aromatic C–H fragment with the metal center [6,7b,20]. The mild conditions required for the reaction of complex **1** with mono and bidentate phosphines induced us to study its reactivity towards the potentially terdentate ligand PCHP, in an attempt to isolate similar species to those mentioned above.

Treatment of **1** with one equivalent of PCHP ligand (CH_2Cl_2; r.t.), affords the binuclear complex [{RuCl$_2$(η^3-NN′N)}$_2$(μ-η^2-PCHP)] in 60% yield (**10**, Fig. 1). The molecular symmetry, reflected in the ^{1}H- and ^{31}P{^{1}H}-NMR spectra of complex **10**, strongly suggest a similar ligand arrangement to that depicted above for complexes **7**–**9**. The resonance corresponding to the phosphorous atoms appears as a singlet at 39.5 ppm, in a similar shift to that observed in other ruthenium complexes containing a co-ordinated PCHP ligand [6]. The NMR data can be found in Tables 1 and 2.

In order to confirm the structure proposed for compound **10**, an X-ray diffraction study on a crystalline sample of **10** has been carried out. Crystal and refinement data are listed in Section 4. A molecular plot and selected bond distances and angles of **10** are given in Fig. 4. The structure displays a similar ligand arrangement to that observed for **8**, with two [RuCl$_2$(NN′N)] moieties linked by the PCHP ligand. The molecule presents approximate C_2 molecular symmetry along the C_{38}–C_{41} axes, in accordance with the data observed in solution (NMR). The Ru–P distances (2.337(2)–2.339(3) Å) are in the range typical of other Ru–*PCP* complexes [6].

As far as we are aware, the only previous examples containing a bridging noncyclometallated PCHP ligand occur in the complexes [Ag$_2$X$_2$(μ-η^2-PCHP)] (X = Cl, I, NO$_3$), in which the ligand bridges between two silver atoms [21]. Complex **10** represents the first example of this co-ordination mode for this ligand in the chemistry of ruthenium. Some Pd and Pt complexes containing the related noncyclometallated ligand 1,3-bis[-(diphenylphosphino)methylene]mesitylene have been recently reported by Milstein et al. [20b]. The isolation and characterization of this type of species is of significant interest since it represents an isolable example of an intermediate complex previously observed only spectroscopically [6].

In an attempt to obtain an orthometallated complex containing the neutral NN′N and the anionic [PCP] ligands, the compound [Ru(OTf)(η^3-NN′N)(PPh$_3$)]-[OTf] [2] was treated with one equivalent of neutral PCHP. However, no reaction was observed after extended time periods at elevated temperature. This behavior is probably due to the electronic effects of the pyridine ligand when compared with the similar $[PCP]^-$ derivative, since the latter readily undergoes orthometallation [6]. When other silver salts containing non-coordinating anions such as $[BF_4]^-$ or $[PF_6]^-$ are used as chlorine anion abstractors, this results in the decomposition of the intermediate species and thus no pure compounds could be obtained.

3. Conclusions

The present work provides a useful synthetic route for the formation of Ru catalyst precursors containing different phosphine ligands. The large variety of phosphine ligands that can be used allows one to tailor the active metal site for applications in a wide range of organic transformations. In addition, the synthesis and characterization of the unusual complex **10** containing a bridging (noncyclometallated) PCHP 'pincer' ligand is of general interest for the elucidation and/or confirmation of previously proposed intermediates in cyclometallation chemistry.

4. Experimental

4.1. General

Solvents were dried over sodium diphenyl ketyl (Et_2O, hydrocarbons) or CaH_2 (CH_2Cl_2, $ClCH_2CH_2Cl$) and distilled under a nitrogen atmosphere prior to use. Unless otherwise stated, the reactions were carried out under an atmosphere of nitrogen at r.t. All reagents were obtained from commercial sources and were used without further purification. Complex **1** was prepared as described previously [2].^{1}H (200 and 300 MHz), $^{13}C\{^{1}H\}$ (50 and 75 MHz) and $^{31}P\{^{1}H\}$ (81 and 121 MHz) NMR spectra were recorded at r.t., with either a Bruker AC-200 or AC-300 instruments, using $SiMe_4$ as internal standard (δ_H or $\delta_C = 0.00$) or external H_3PO_4 (85%, $\delta_P = 0.00$). Fast atom bombardment mass spectra (FAB MS) were obtained from the Analytical Chemical Department of Utrecht University on a JEOL JMS SX/SX 102A four-sector mass spectrometer, using nitrobenzyl alcohol as matrix and xenon as bombarding gas. Microanalyses were obtained from H. Kolbe Mikroanalytisches Laboratorium (Germany). Molecular calculations (MM2) were made with the CAChe

Table 2
Selected $^{13}C\{^{1}H\}$-NMR data of compounds **2**–**10** [a,b,c,d,e]

Compound	NN′N ligand					Other signals
	o-C	*m*-C	*p*-C	CH_2	NMe_2	
2	161.7	119.3	135.0	73.7	45.6	–
3	160.8	119.5	135.1	73.4	54.9	–
4	161.0	119.4	134.2	73.2	55.6	17.8(d, 23.5) [f]
5	160.6	119.6	136.1	73.0	55.8	52.2(d, 6.24) [g]
6	161.7	120.4	136.9	70.7, 65.2	54.0, 45.0	54.8(t, 19.7) [h]
7	161.3	120.4	138.5	73.5	54.9	22.0(m, br) [i]
8	161.5	119.3	134.6	73.7	55.3	20.2(m, br) [j], 27.0(m, br) [k]
9	159.9	117.0	136.6	71.6	52.8	19.5 [l], 69.7(d, 6.6) [m], 74.4(d, 9.4) [n], 84.3(d, 26.5) [o]
10	161.6	119.1	135.1	73.5	54.5	34.1(d, 14.6) [p], 126.0 [q], 127.2 [r], 133.8(t, 2.5) [s], 134.6(d, 2.7) [t]

[a] Spectra recorded using CD_2Cl_2 as solvent.
[b] All signals are singlets unless otherwise stated.
[c] Key: d, doublet; t, triplet; br, broad.
[d] Coupling constants (parentheses) in Hertz.
[e] All the signals corresponding to the phenyl rings have been omitted for simplicity.
[f] $P(CH_3)_3$.
[g] $P(OCH_3)_3$.
[h] CH_2.
[i] CH_2.
[j] $CH_2CH_2CH_2$.
[k] $CH_2CH_2CH_2$.
[l] $P[p\text{-}(C_6H_4CH_3)_2]$.
[m] *m*-*C*H, Cp ring.
[n] *o*-*C*H, Cp ring.
[o] *ipso*-*C*, Cp ring.
[p] *C*H$_2$.
[q] *o*-*C*H.
[r] *p*-*C*H.
[s] *o*-*C*H respect to both phosphorous.
[t] *ipso*-*C*.

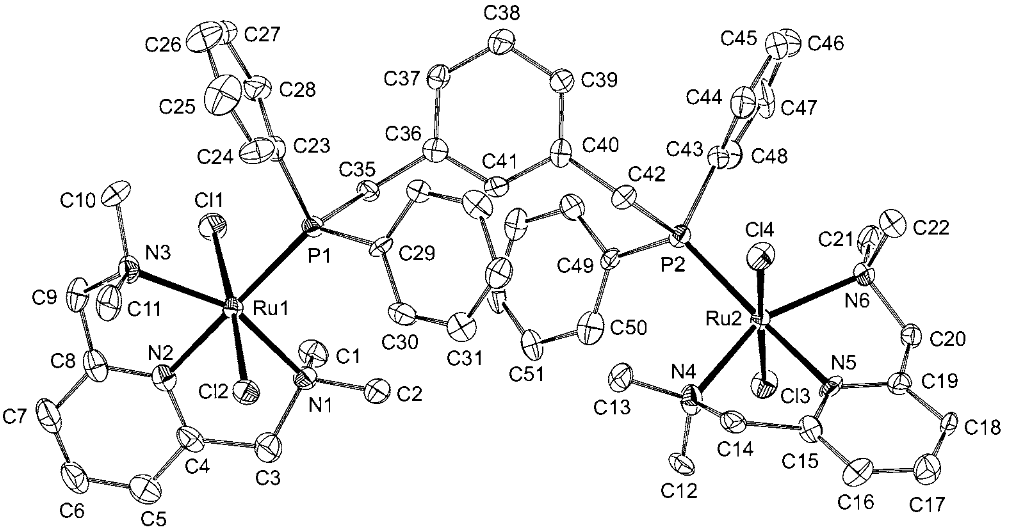


Fig. 4. Molecular structure of compound **10**. Displacement ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å), angles (°) and torsion angles (°): Ru(1)–Cl(1) 2.441(2), Ru(1)–Cl(2) 2.422(2), Ru(2)–Cl(3) 2.432(2), Ru(2)–Cl(4) 2.428(2), Ru(1)–N(1) 2.227(6), Ru(1)–N(2) 2.034(7), Ru(1)–N(3) 2.223(7), Ru(2)–N(4) 2.246(7), Ru(2)–N(5) 2.044(7), Ru(2)–N(6) 2.243(7), Ru(1)–P(1) 2.339(2), Ru(2)–P(2) 2.337(2); Cl(1)–Ru(1)–Cl(2) 176.54(8), Cl(3)–Ru(2)–Cl(4) 177.87(8), N(1)–Ru(1)–N(3) 155.6(3), N(4)–Ru(2)–N(6) 154.2(2), N(2)–Ru(1)–P(1) 178.3(2), N(5)–Ru(2)–P(2) 175.0(2), Ru(1)–P(1)–C(35) 109.0(3), Ru(2)–P(2)–C(42) 112.6(3), P(1)–C(35)–C(36) 120.0(6), P(2)–C(42)–C(40) 118.8(5), C(35)–C(36)–C(41) 119.3(8), C(42)–C(40)–C(41) 118.9(8); N(1)–C(3)–C(4)–N(2) −26.2(11), N(2)–C(8)–C(9)–N(3) −31.6(11), N(4)–C(14)–C(15)–N(5) 28.4(10), N(5)–C(19)–C(20)–N(6) 35.4(10), P(1)–C(35)–C(36)–C(41) 80.4(9), P(2)–C(42)–C(40)–C(41) 84.9(9).

program package (Oxford Molecular Group). Pertinent NMR data of complexes **2**–**10** are reported in Tables 1 and 2.

4.2. Syntheses

*4.2.1. [RuCl$_2$(η^3-NN′N)(PPh$_3$)] (**2**)*

An excess of triphenylphosphine (100 mg, 0.382 mmol) was added to a solution of **1** (140 mg, 0.185 mmol) in CH_2Cl_2 (30 ml) and the mixture was then stirred at reflux temperature for 45 min. The color of the mixture changed from orange to red. The solvent was removed under reduced pressure and the residue washed with Et_2O/pentane (1:5, 2 × 20 ml) to give **2** as an orange solid (170 mg, 71%). Its analytical and spectroscopic data matched those reported in the literature [2].

*4.2.2. [RuCl$_2$(η^3-NN′N)(PHPh$_2$)] (**3**)*

Diphenylphosphine (91.8 μl, 0.527 mmol) was added to a solution of **1** (200 mg, 0.264 mmol) in CH_2Cl_2 (20 ml) and the mixture was then stirred for 45 min. The color of the solution changed from orange to red. The solvent was removed under reduced pressure and the residue washed with pentane (3 × 30 ml) to give **3** as an orange solid (250 mg, 86%). FAB MS (*m*/*z*): 551 [M$^+$]; $C_{23}H_{30}Cl_2N_3PRu$ (551): Calc. C 50.09, H 5.48, N 7.62; Found C 49.86, H 5.44, N 7.63.

*4.2.3. [RuCl$_2$(η^3-NN′N)(PMe$_3$)] (**4**)*

Trimethylphosphine (292.6 μl 1.0 M in toluene, 0.293 mmol) was added to a solution of **1** (111 mg, 0.146 mmol) in CH_2Cl_2 (30 ml) and the mixture was then stirred for 1 h. The mixture changed color from orange to light brown. The solvent was removed under reduced pressure and the residue washed with pentane (10 ml) to give **4** as a pale brown solid (105 mg, 81%). FAB MS (*m*/*z*): 441 [M$^+$]; $C_{14}H_{28}Cl_2N_3PRu$ (441): Calc. C 38.10, H 5.39, N 9.52; Found C 37.61, H 5.58, N 9.10.

*4.2.4. [RuCl$_2$(η^3-NN′N)(P(OMe)$_3$)] (**5**)*

Trimethylphosphite (62.2 μl, 0.527 mmol) was added to a solution of **1** (200 mg, 0.263 mmol) in CH_2Cl_2 (40 ml) and the mixture was then stirred for 90 min, changing the color from orange to light brown. The solvent was removed under reduced pressure and the residue washed with pentane (2 × 20 ml) to give **5** as a pale brown solid (220 mg, 85%). FAB MS (*m*/*z*): 489 [M$^+$]; $C_{14}H_{28}Cl_2N_3O_3PRu$ (489): Calc. C 34.36, H 5.77, N 8.59; Found C 34.48, H 5.71, N 8.48.

*4.2.5. [RuCl$_2$(η^2-NN′N)(η^2-dppm)] (**6**)*

Bis(diphenylphosphino)methane (255.4 mg, 0.666 mmol) was added to a solution of **1** (252 mg, 0.333 mmol) in CH_2Cl_2 (30 ml) and the mixture was then stirred for 60 min. The color of the solution changed from orange to light brown. The solvent was removed under reduced pressure and the residue washed with Et_2O (2 × 20 ml) to give **6** as a brown solid (320 mg, 64%). FAB MS (m/z): 750 [M^+]; $C_{36}H_{41}Cl_2N_3P_2Ru$ (749.7): Calc. C 57.68, H 5.51, N 5.61; Found C 58.01, H 5.72, N 5.35.

4.2.6. [{RuCl$_2$(η^3-NN′N)}$_2$(μ-dppe)] (**7**)

1,2-Bis(diphenylphosphino)ethane (119.6 mg, 0.300 mmol) was added to a solution of **1** (228 mg, 0.300 mmol) in CH_2Cl_2 (40 ml) and the mixture was then stirred for 60 min (color changed from orange to red). The solvent was removed under reduced pressure and the residue washed with Et_2O (2 × 20 ml) to give **7** as a red solid (280 mg, 83%). FAB MS (m/z): 1129 [M^+]; $C_{48}H_{62}Cl_4N_6P_2Ru_2$ (1129): Calc. C 51.06, H 5.54, N 7.44; Found C 51.30, H 5.62, N 7.37.

4.2.7. [{RuCl$_2$(η^3-NN′N)}$_2$(μ-dppp)] (**8**)

1,3-Bis(diphenylphosphino)propane (244.4 mg, 0.593 mmol) was added to a solution of **1** (450 mg, 0.593 mmol) in CH_2Cl_2 (40 ml) and the mixture was then stirred for 60 min (color changed from orange to red). The solvent was removed under reduced pressure and the residue washed with Et_2O (2 × 20 ml) to give **8** as a red solid (600 mg, 89%). FAB MS (m/z): 1143 [M^+]; $C_{49}H_{64}Cl_4N_6P_2Ru_2$ (1143): Calc. C 51.49, H 5.64, N 7.35; Found C 51.70, H 5.72, N 7.09.

4.2.8. [{RuCl$_2$(η^3-NN′N)}$_2$(μ-dtpf)] (**9**)

1,1′-Bis[di(p-tolyl)phosphino]ferrocene (dtpf, 241.2 mg, 0.396 mmol) was added to a solution of **1** (300 mg, 0.396 mmol) in CH_2Cl_2 (20 ml) and the mixture was then stirred for 60 min. The color changed from orange to dark red. The solvent was removed under reduced pressure and the residue washed with Et_2O (3 × 20 ml) to give **9** as an orange solid (400 mg, 60%). $C_{81}H_{74}Cl_4FeN_6P_2Ru_2$ (1677.4): Calc. C 58.00, H 4.45, N 5.01; Found C 57.78, H 4.36, N 4.89.

4.2.9. [{RuCl$_2$(η^3-NN′N)}$_2$(μ-η^2-PCHP)] (**10**)

1,3-Bis[(diphenylphosphino)methyl]benzene (196 mg, 0.308 mmol) was added to a solution of **1** (234 mg, 0.308 mmol) in CH_2Cl_2 (20 ml) and the mixture was then stirred for 60 min. The color of the mixture changed from orange to red. The solvent was removed under reduced pressure and the residue washed with Et_2O (2 × 20 ml) to give **10** as a red solid (280 mg, 75%). FAB MS (m/z): 1169 [$M^+ - Cl$]; $C_{54}H_{66}Cl_4N_6P_2Ru_2$·(1205.1): Calc. C 53.82, H 5.52, N 6.97, P 5.14; Found C 53.66, H 5.56, N 6.75, P 5.06.

4.3. Crystal structure of **8** · CH_2Cl_2 · C_6H_6

A red crystal obtained by layering ether on a solution of the complex in dichloromethane/benzene was used for the X-ray diffraction study. Molecular formula: $C_{49}H_{64}Cl_4N_6P_2Ru_2 \cdot CH_2Cl_2 \cdot C_6H_6$, $M_r = 1305.98$, triclinic, $P\bar{1}$ (no. 2), $a = 13.755(4)$, $b = 15.147(4)$, $c = 15.377(3)$ Å, $\alpha = 68.361(16)$, $\beta = 85.23(2)$, $\gamma = 72.63(2)°$, $V = 2840.9(12)$ Å^3, $Z = 2$, $D_{calc} = 1.527$ g cm^{-3}, $\mu = 0.91$ mm^{-1}, $T = 150(2)$ K, $(\sin \vartheta/\lambda)_{max} = 0.650$ Å^{-1}, red plates 0.10 × 0.35 × 0.43 mm, measured reflections: 18663, unique reflections: 13040 ($R_{int} = 0.038$), R-values ($I > 2\sigma I$): $R_1 = 0.0500$, $wR_2 = 0.1057$, all data: $R_1 = 0.0832$, $wR_2 = 0.1190$. Diffractometer: Enraf-Nonius CAD4T with rotating anode (Mo–K$_\alpha$, $\lambda = 0.71073$ Å). Structure solution with Patterson-methods (DIRDIF-96) [22]. Structure refinement with SHELXL-97 [23] against F^2. 909 parameters. Nonhydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were refined freely with isotropic displacement parameters and in the disordered benzene molecule as rigid groups. Structure graphics, checking for higher symmetry and absorption correction (Psiscams, 0.83–0.97 transmission) were performed with the program PLATON [24]. Crystallographic data can be obtained from the authors.

4.4. Crystal structure of **10** · 2CH_2Cl_2

A dark orange crystal obtained by layering ether on a solution of the complex in dichloromethane/benzene was used for the X-ray diffraction study. Molecular formula: $C_{54}H_{66}Cl_4N_6P_2Ru_2 \cdot 2CH_2Cl_2$, $M_r = 1374.86$, monoclinic, $P2_1/c$ (no. 14), $a = 16.687(4)$, $b = 14.594(4)$, $c = 24.725(3)$ Å, $\beta = 100.55(3)°$, $V = 5919(2)$ Å^3, $Z = 4$, $D_{calc.} = 1.543$ g cm^{-3}, $\mu = 0.968$ mm^{-1}, $T = 150(2)$ K, $(\sin \vartheta/\lambda)_{max} = 0.572$ Å^{-1}, dark orange plates 0.08 × 0.38 × 0.38 mm, measured reflections: 18585, unique reflections: 9296 ($R_{int} = 0.11$), R-values ($I > 2\sigma I$): $R_1 = 0.0622$, $wR_2 = 0.1149$, all data: $R_1 = 0.1283$, $wR_2 = 0.1373$. Diffractometer: Enraf-Nonius CAD4T with rotating anode (Mo–K$_\alpha$, $\lambda = 0.71073$ Å). Structure solution with Patterson-methods (DIRDIF-96) [22]. Structure refinement with SHELXL-97 [23] against F^2. 667 parameters. Nonhydrogen atoms were refined with anisotropic temperature parameters, hydrogen atoms were refined as rigid groups. Structure graphics, checking for higher symmetry and absorption correction (routine DELABS, 0.43–0.81 transmission) were performed with the program PLATON [24]. Crystallographic data can be obtained from the authors.

5. Supplementary material

Tables of atomic co-ordinates, bond distances and angles, anisotropic thermal parameters, and H atom co-ordinates for **8** · CH_2Cl_2 · C_6H_6 and **10** · 2 CH_2Cl_2 are available from the authors.

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