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Double Carbon–Hydrogen Activation of 2-Vinylpyridine: Synthesis of Tri- and Pentanuclear Clusters Containing the μ-NC5H4CH═C Ligand

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Synopsis

Triruthenium carbonyls react with 2-vinylpyridene, leading to a previously unknown double carbon–hydrogen bond activation of the β-carbon of the vinyl group to afford a dimetalated 2-vinylpyridyl ligand which can adopt different coordination modes.

Abstract
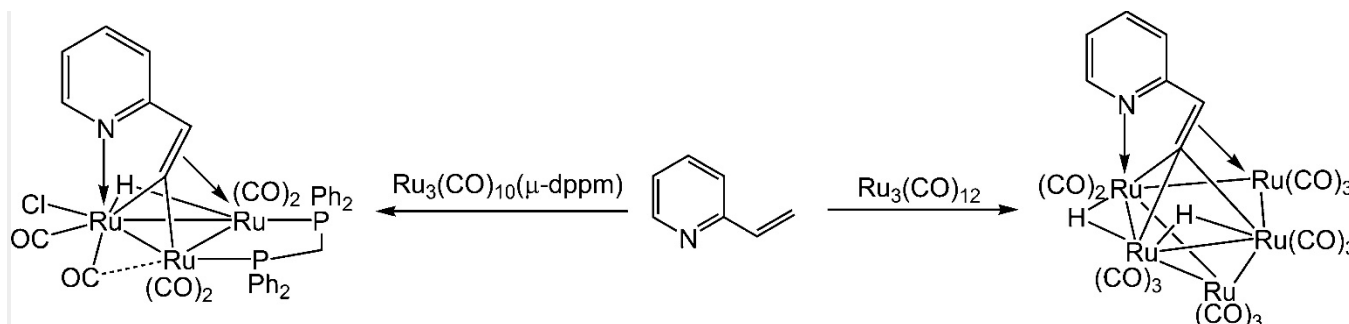
Reactions of 2-vinylpyridine with the triruthenium complexes [$Ru_3(CO)_{12}$] and [$Ru_3(CO)_{10}(\mu\text{-dppm})$] leads to a previously unknown double carbon–hydrogen bond activation of the β-carbon of the vinyl group to afford the pentaruthenium and triruthenium complexes [$Ru_5(CO)_{14}(\mu_4\text{-}C_5H_4CH\text{=}C)(\mu\text{-}H)_2$] (**1**) and [$Ru_3Cl(CO)_5(\mu\text{-CO})(\mu\text{-dppm})(\mu_3\text{-}NC_5H_4CH\text{=}C)(\mu\text{-}H)$] (**2**), respectively. Crystal structures reveal two different forms of bridging of the dimetalated 2-vinylpyridyl ligand, capping a square face in **1** and a triangular face in **2**.

Cyclometalation is an important process, due to its relevance to the selective activation and functionalization of hydrocarbons and also its importance in catalysis and in the preparation of organometallic compounds.[1-4] 2-Vinylpyridine is a versatile ligand which has been widely used to stabilize transition-metal–carbon bonds in a chelating coordination mode, the latter being believed to play a key role in catalysis.[5] The reactivity of 2-vinylpyridine with a variety of mononuclear complexes has been studied extensively in recent years,[6-11] and a number of binding modes (A–C) have been established (Chart). In many cases initial coordination of 2-vinylpyridine takes place via the nitrogen atom (A) followed by secondary binding of the vinyl group (B) if there is a second vacant coordination site. The latter often leads to oxidative addition of a carbon–hydrogen bond to afford cyclometalated complexes (C), a binding mode that is extremely common.[4]
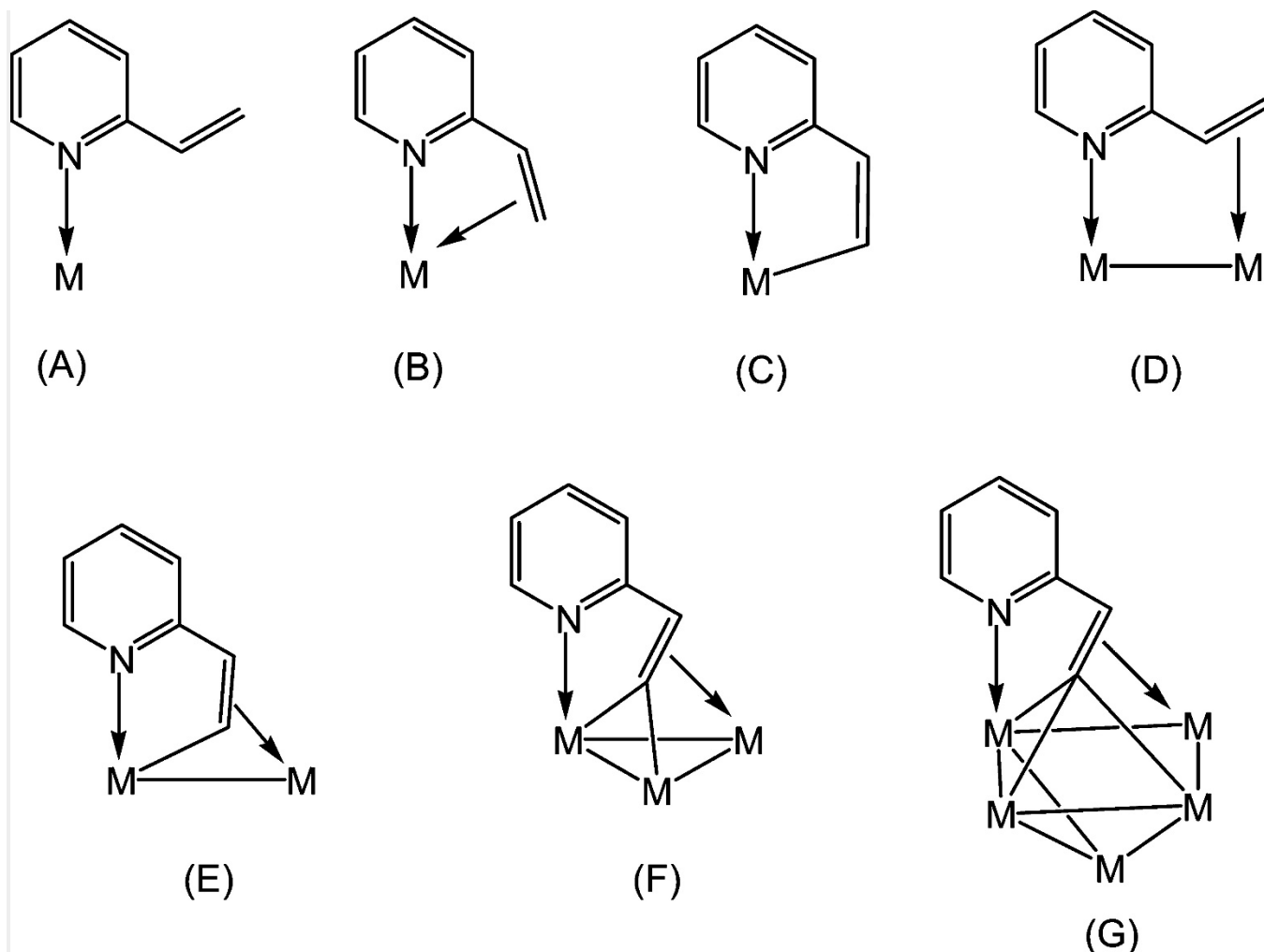
Chart 1

At a polynuclear center, binding of the nitrogen and vinyl moieties need not occur to the same metal atom (D), the recent isolation of $[Re_2(CO)_8(\mu\text{-}NC_5H_4CH=CH_2)]$ being a good example of this behavior.[12] Cyclometalation can also occur at polynuclear metal centers, the cyclometalated ligand typically bridging two metal atoms (E). The first example of this was reported in the mid 1980s by Deeming and co-workers.[13] The reaction of 2-vinylpyridine with $[Os_3(CO)_{10}(\mu\text{-}H)_2]$ or $[Os_3(CO)_{10}(MeCN)_2]$ leads to the formation of the cyclometalated cluster $[Os_3(CO)_{10}(\mu\text{-}NC_5H_4CH=CH)(\mu\text{-}H)]$, while a phosphine derivative, $[Os_3(CO)_9(PMe_2Ph)(\mu\text{-}NC_5H_4CH=CH)(\mu\text{-}H)]$, was the major product upon addition of 2-vinylpyridine to $[Os_3(CO)_9(PMe_2Ph)(\mu\text{-}H)_2]$.[13] More recently, similar binding modes have been reported in $[Os_6(CO)_{20}(\mu\text{-}NC_5H_4CH=CH)(\mu\text{-}H)]$[14] and $[Os_4Rh(CO)_{13}(\mu\text{-}NC_5H_4CH=CH)(\mu\text{-}H)_4]$.[15] In all of these examples, the metalated ligand binds only to two metal atoms. We now report our studies on the reactivity of $[Ru_3(CO)_{12}]$ and $[Ru_3(CO)_{10}(\mu\text{-}dppm)]$ with 2-vinylpyridine, the aim of which was to prepare triruthenium clusters with a cyclometalated 2-vinylpyridine ligand, since it has been reported that such compounds may have important implications in catalysis. We have found, however, that dimetalated 2-vinylpyridine-containing clusters are obtained in both instances, the precise ligand binding modes (F and G) varying with the cluster nuclearity. As far as we are aware, this is the first report of the double carbon–hydrogen bond activation of 2-vinylpyridine.

Results and Discussion

Heating 2-vinylpyridine with [$Ru_3(CO)_{12}$] in refluxing THF afforded the pentaruthenium cluster [$Ru_5(CO)_{14}(\mu_4$-$NC_5H_4CH\!\!=\!\!C)(\mu$-H)$_2$] (**1**) in moderate yields after thin-layer chromatography (eq 1). Characterization was made by a combination of spectroscopic data and single-crystal X-ray diffraction studies. Clear evidence for the double carbon–hydrogen bond cleavage of the 2-vinylpyridyl ligand comes from the ¹H NMR spectrum, in which a hydride resonance was observed at δ −21.28 integrating to two protons. Four further signals were also seen in the aromatic region of the spectrum together with a singlet at δ 4.76, each being associated with a single proton. In the mass spectrum, an ion at *m/z* 1004 suggested a pentanuclear ruthenium framework; however, full elucidation of the cluster core geometry was only obtained via a crystallographic study, the results of which are summarized in Figure 1 and its caption.

(1)

(1)
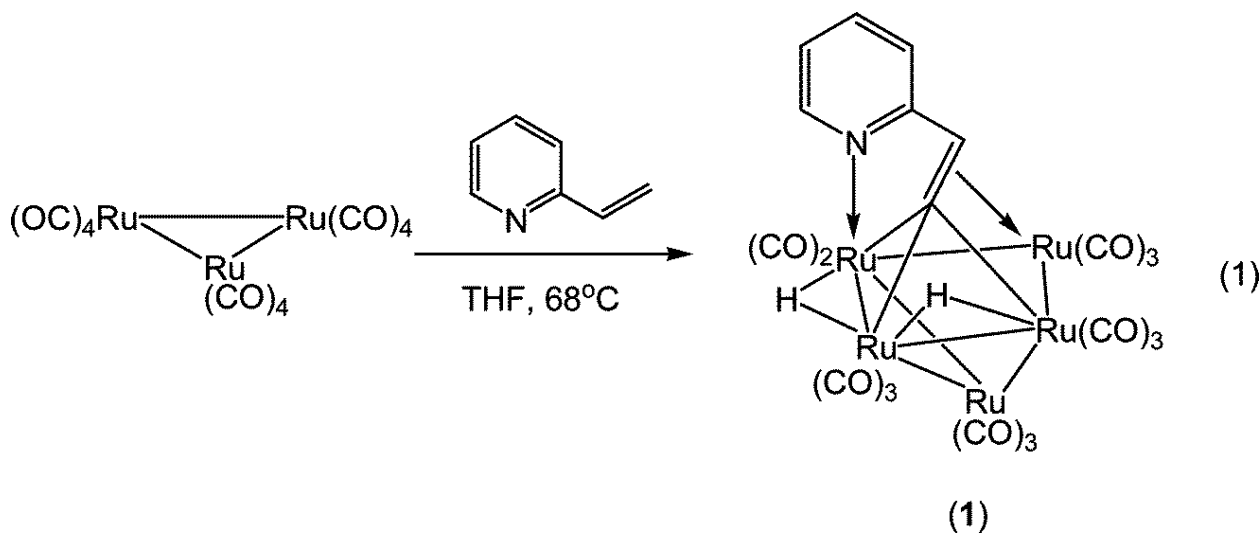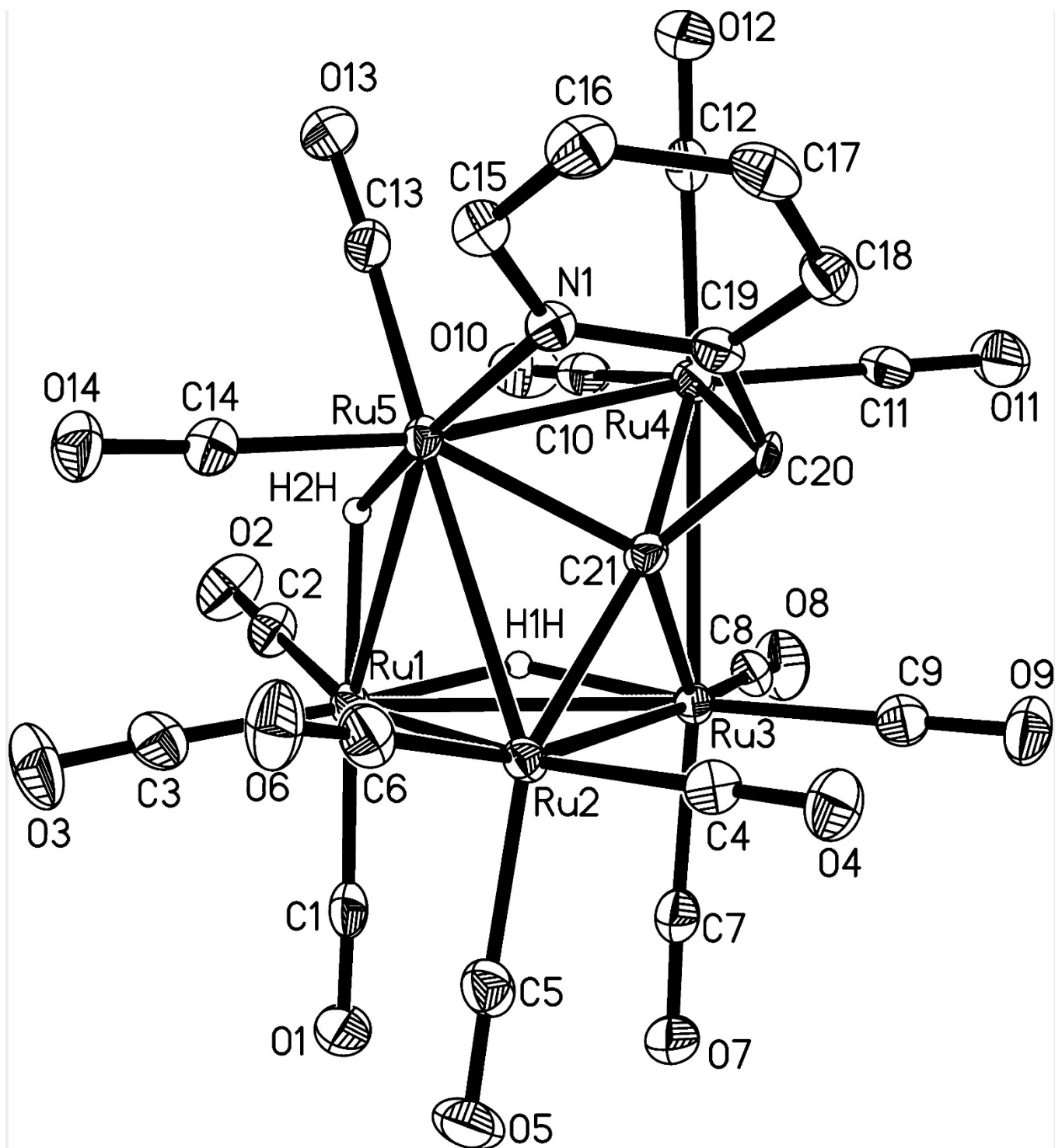
Figure 1. ORTEP view of the molecular structure of **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ru(1)−Ru(2) = 2.7799(4), Ru(1)−Ru(5) = 2.9661(4), Ru(1)−Ru(3) = 3.0376(4), Ru(2)−Ru(3) = 2.8188(4), Ru(2)−Ru(5) = 2.8652(4), Ru(3)−Ru(4) = 2.8615(4), Ru(4)−Ru(5) = 2.8409(4), Ru(5)−N(1) = 2.119(3), Ru(2)−C(21) = 2.114(4), Ru(3)−C(21) = 2.152(4), Ru(4)−C(21) = 2.090(4), Ru(4)−C(20) = 2.156(4), C(20)−C(21) = 1.437(6), Ru(5)−C(21) = 2.122(4); Ru(2)−Ru(1)−Ru(5) = 59.72(1), Ru(2)−Ru(1)−Ru(3) = 57.76(1), Ru(5)−Ru(1)−Ru(3) = 77.23(1), Ru(1)−Ru(2)−Ru(3) =

65.71(1), Ru(1)−Ru(2)−Ru(5) = 63.37(1), Ru(3)−Ru(2)−Ru(5) = 82.49(1), Ru(2)−Ru(3)−Ru(4) = 92.86(1), Ru(2)−Ru(3)−Ru(1) = 56.53(1), Ru(4)−Ru(3)−Ru(1) = 89.83(1), Ru(5)−Ru(4)−Ru(3) = 82.17(1), Ru(4)−C(21)−Ru(2) = 156.4(2), Ru(4)−C(21)−Ru(5) = 84.8(1), Ru(2)−C(21)−Ru(5) = 85.1(2), Ru(4)−C(21)−Ru(3) = 84.8(1), Ru(2)−C(21)−Ru(3) = 82.7(1), Ru(5)−C(21)−Ru(3) = 122.5(2), C(21)−Ru(4)−C(20) = 39.5(2).

As far as we are aware, **1** represents a unique example of an open pentaruthenium cluster, whereby the wingtips (Ru(3) and Ru(5)) of a butterfly arrangement of four metal atoms are bridged by a fifth (Ru(4)). A square face of this arrangement (Ru(2)Ru(3)Ru(4)Ru(5)) is capped by the new dimetalated 2-vinylpyridine (NC$_5$H$_4$CH=C) ligand formed upon oxidative addition of both carbon−hydrogen bonds of the terminal carbon atom of the vinyl group. The metalated carbon atom, C(21), bridges four ruthenium atoms; the ruthenium−carbon bonds vary between 2.090(4) and 2.152(4) Å, the shortest of which is to Ru(4). The latter is also bonded to the second carbon of the vinyl group (Ru(4)−C(20) = 2.156(4) Å), the carbon−carbon bond of which is now 1.437(6) Å. This can be compared to a similar bond length of 1.424(22) Å found in the single metalated ligand in [Os$_3$(CO)$_9$(PMe$_2$Ph)(μ-NC$_5$H$_4$CH=CH)(μ-H)].[13] The nitrogen atom is also bound to the square face, the Ru(5)−N(1) distance of 2.119(3) Å being close to similar bonds in [Ru$_3$(CO)$_9$(PPh$_3$)(μ-NC$_5$H$_4$)(μ-H)] (2.103(6) Å)[16] and [Ru$_3$(CO)$_{10}$(μ-NC$_5$H$_4$)(μ-H)] (2.111(4) Å).[17] A somewhat related example of a pentaruthenium cluster containing a quadruply bridging ligand is [Ru$_5$(CO)$_{14}$(μ$_4$-C$_3$H$_2$Ph)(μ$_3$-H)], obtained from the reaction of [Ru$_3$(CO)$_{12}$] and isopropylbenzene.[18] The hydrides in **1** were located and refined in the structural analysis. These bridge the Ru(1)−Ru(5) and Ru(1)−Ru(3) edges, which are significantly elongated (2.9661(4) and 3.0376(4) Å, respectively), as is typically found for bridging hydride ligands.[19] The hinge bond (Ru(1)−Ru(2) = 2.7799(4) Å) is significantly shorter than the other metal−metal bonds. The metalated vinylpyridine ligand acts as a 6-electron donor, and thus cluster **1** contains a total of 76 cluster valence electrons and is electron precise on the basis of a total of 7 metal−metal bonds. The mode of formation of **1** is unclear. It was the major product of the reaction, and no significant intermediates were observed when the reaction was monitored by IR spectroscopy. Further, attempts to maintain the trinuclear cluster core by using the activated cluster [Ru$_3$(CO)$_{10}$(MeCN)$_2$] or adding Me$_3$NO did not lead to the generation of other products, and it seemed that a minimum of four metal atoms might be required to stabilize the dimetalated 2-vinylpyridine ligand.

In order to test this hypothesis, we sought to stabilize the triruthenium framework toward fragmentation and investigated the reaction of 2-vinylpyridine with [Ru$_3$(CO)$_{10}$(μ-dppm)], since the diphosphine has been shown to activate the triruthenium core while maintaining the integrity of the trinuclear framework.[20] Treatment of [Ru$_3$(CO)$_{10}$(μ-dppm)] with 2-vinylpyridine in refluxing THF afforded the triruthenium compound [Ru$_3$Cl(CO)$_5$(μ-CO)(μ-dppm)(μ$_3$-NC$_5$H$_4$CH=C)(μ-H)] (**2**) in 30% yield after chromatography (eq 2).

(2)

(**2**)
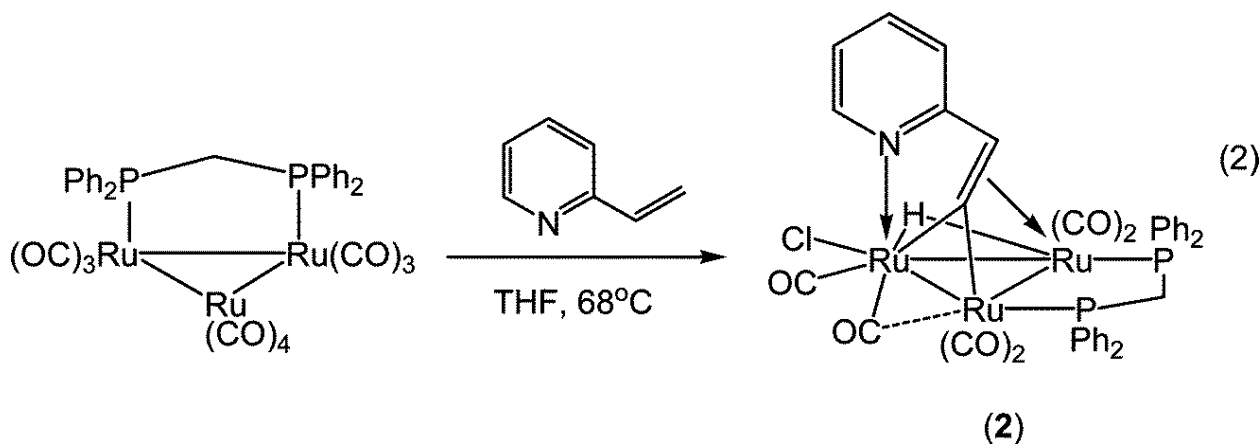
The molecular structure of **2** is depicted in Figure 2, and selected bond distances and angles are listed in the caption. The molecule consists of a triruthenium cluster with five terminal and one semibridging carbonyl ligand, bridging diphosphine and hydrides, a terminal chloride, and a triply bridging dimetalated 2-vinylpyridyl ligand. The latter binds to a face of the ruthenium triangle, being coordinated to one ruthenium through the nitrogen (Ru(3)−N(1) = 2.155(2) Å). The dimetalated carbon, C(13), caps the face quite asymmetrically; ruthenium−carbon bonds vary between 1.953(2) and 2.163(2) Å, the longest being to Ru(1), which is also coordinated to the second vinylic carbon (Ru(1)−C(12) = 2.329(2) Å). The C(12)−C(13) bond distance of 1.399(3) Å is now considerably shorter than that found in **1**, being more typical of a coordinated carbon−carbon double bond. The cluster has one long and two short ruthenium−ruthenium distances, the hydride being crystallographically located (not refined) across the relatively long Ru(1)−Ru(3) edge. The Ru−P distances (Ru(1)−P(1) = 2.3193(6) Å, Ru(2)−P(2) = 2.2862(6) Å) are comparable to those found in $[Ru_3(CO)_{10}(\mu\text{-dppm})]$,(21) and the chloride is equatorially coordinated to the nitrogen-bound ruthenium atom, the Ru(3)−Cl(1) distance of 2.4675(6) Å being typical.(22)
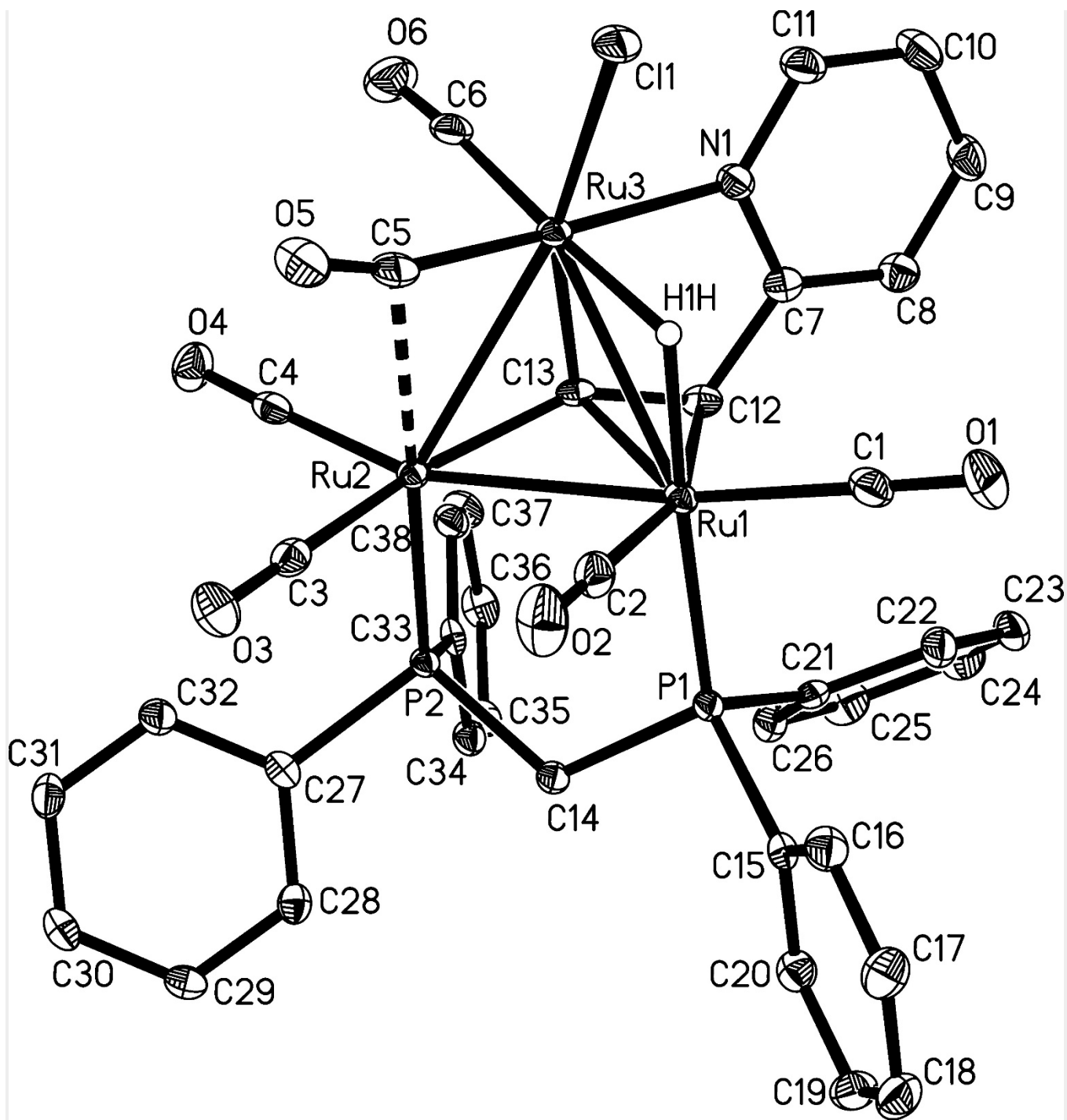
Figure 2. ORTEP view of the molecular structure of **2** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected interatomic distances (Å) and angles (deg): Ru(1)−Ru(2) = 2.8104(2), Ru(1)−Ru(3) = 2.8815(3), Ru(2)−Ru(3) = 2.8397(2), Ru(1)−P(1) = 2.3193(6), Ru(2)−P(2) = 2.2862(6), Ru(3)−N(1) = 2.1545(19), Ru(1)−C(12) = 2.329(2), Ru(1)−C(13) = 2.163(2), Ru(2)−C(13) = 1.953(2), Ru(3)−C(13) = 2.060(2), Ru(2)−C(5) = 2.622(2), Ru(3)−C(5) = 1.909(3), C(12)−C(13) = 1.399(3); Ru(1)−Ru(2)−Ru(3) = 1.324(6), Ru(2)−Ru(1)−Ru(3) = 59.838(6), Ru(2)−Ru(3)−Ru(1) = 58.838(6), P(1)−C(14)−P(2) = 116.6(1), Ru(2)−C(13)−Ru(3) = 90.05(9), Ru(2)−C(13)−Ru(1) = 85.98(9), Ru(3)−C(13)−Ru(1) = 86.04(8).

Spectroscopic data are consistent with the formulation. In the ^{1}H NMR spectrum, the vinylic proton appears as a singlet at δ 4.28 and the hydride is seen at δ −16.89 (d, J = 12.4 Hz). In the ^{31}P NMR spectrum two doublets are observed at 51.9 and 34.3 ppm (J_{PP} = 53.2 Hz), and in the mass spectrum a parent ion (m/z 997) is observed. The origin of the chloride in **2** is unclear, although one can envisage the initial formation of an intermediate with both bridging and terminal hydrides. The latter are known to exchange with chloride during chromatography or crystallization. Attempts to identify such a species prior to chromatography were unsuccessful. The dimetalated 2-vinylpyridine ligand again acts as a 6-electron donor, and on the assumption that the chloride donates only a single electron, then **2** contains a total of 48 valence electrons and is electron precise on the basis of 3 metal−metal bonds.

We have probed the binding of the dimetalated 2-vinylpyridine ligands in **1** and **2** using density functional theory (DFT).(23) In **1**, according to the natural bonding orbital (NBO) method,(24) the dimetalated carbon, C(21), bonds to all four ruthenium atoms in the square in an almost even manner, donating electrons to all four through an orbital totally localized on C(21). This atom also has a two-center bonding orbital with C(20), which accounts for the single carbon−carbon bond between the two atoms. Confirming X-ray data, NBO calculations on **2** show that C(13) is more asymmetrically bonded and has a double bond with C(12). Two two-center bonding orbitals are present between C(13) and Ru(2) and Ru(3), while the C(13)−C(12) double bond donates electrons to Ru(1). Furthermore, according to NBO analysis, the chloride is donating two electrons to Ru(3).

In summary, we have shown that 2-vinylpyridine reacts with ruthenium carbonyl clusters to give a previously unreported dimetalated ligand, which can bind to the cluster core in two different ways. This reactivity is significantly different from that seen in related triosmium chemistry, in which only a single metalation is observed. This may be due to the more facile oxidative addition of carbon−hydrogen bonds at ruthenium versus osmium centers, or it may simply be that the second metalation has a higher activation barrier in the related osmium complexes and the reaction conditions used by Deeming and co-workers in their triosmium work (50 °C in hexane) were not forcing enough to drive the reaction to completion.(13) The formation of trinuclear **2** from [Ru$_3$(CO)$_{10}$(μ-dppm)] provides a further example of the utility of this small-bite-angle diphosphine in acting as an efficient ligand toward maintaining the integrity of the trinuclear framework, which is so frequently disrupted in the analogous chemistry of [Ru$_3$(CO)$_{12}$].

Experimental Section

All reactions were carried out under a nitrogen atmosphere using dried and degassed solvents. ^{1}H and ^{31}P NMR spectra were measured on a Bruker DPX 400 spectrometer. 2-Vinylpyridine was purchased from Aldrich and used as received. The cluster [Ru$_3$(CO)$_{10}$(μ-dppm)] was prepared according to the published procedure.(25) Crystallographic data for the structural analysis of **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC 666124 and 666123. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, + 44-1223-336033; email, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

Synthesis of 1

A THF solution (25 mL) of [Ru$_3$(CO)$_{12}$] (100 mg, 0.156 mmol) and 2-vinylpyridine (25 mg, 0.234 mmol) was heated to reflux for 2.5 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane/CH$_2$Cl$_2$ (9/1 v/v) afforded [Ru$_5$(CO)$_{14}$(μ$_4$-η[1]:η[2]:η[1]-NC$_5$H$_4$CH═C)(μ-H)$_2$] (**1**; 35 mg, 24%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. Anal. Calcd for C$_{21}$H$_7$N$_1$O$_{14}$Ru$_5$: C, 25.16; H, 0.70; N, 1.40. Found: C, 25.42; H, 1.05; N, 1.53. IR (v(CO); CH$_2$Cl$_2$): 2095 s, 2068 vs, 2056 vs, 2043 vs, 2011 vs, 1992 m,

1975 w, 1959 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.19 (d, J = 5.8 Hz, 1H), 7.43 (t, J = 5.8 Hz, 1H), 7.23 (d, J = 5.8 Hz, 1H), 6.66 (t, J = 5.8 Hz, 1H), 4.76 (s, 1H), −21.28 (s, 2H). MS (FAB): m/z 1004 (M$^+$).

Synthesis of 2

To a THF solution (25 mL) of [Ru$_3$(CO)$_{10}$(μ-dppm)] (100 mg, 0.103 mmol) was added 2-vinylpyridine (16 mg, 0.155 mmol), and the reaction solution was refluxed for 14.5 h. After removal of the solvent under reduced pressure, the residue was chromatographed by TLC on silica gel. Elution with hexane/CH$_2$Cl$_2$ (9/1 v/v) afforded [Ru$_3$Cl(CO)$_5$(μ-CO)(μ-dppm)(μ$_3$-NC$_5$H$_4$CH=C)(μ-H)] (**2**·CH$_2$Cl$_2$; 50 mg, 30%) as red crystals after recrystallization from hexane/CH$_2$Cl$_2$ at 4 °C. Anal. Calcd for C$_{39}$H$_{30}$Cl$_3$N$_1$O$_6$P$_2$Ru$_3$: C, 36.53; H, 2.36; N, 1.09. Found: C, 36.82; H, 2.58; N, 1.15. IR (v(CO); CH$_2$Cl$_2$): 2039 vs, 2011 vs, 1996 vs, 1969 s, 1942 w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.07 (d, J= 5.6 Hz, 1H), 7.93 (t, J = 5.6 Hz, 1H), 7.57−7.41 (m, 20H), 7.12 (t, J = 5.6 Hz, 1H), 6.56 (d, J = 5.6 Hz, 1H), 4.39 (m, 1H), 4.28 (s, 1H), 3.32 (m, 1H), −16.89 (d, J = 12.4 Hz, 1H). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 51.9 (d, J = 53.2 Hz), 34.3 (d, J = 53.2 Hz). MS (FAB): m/z 997 (M$^+$).

Crystal Structure Determinations

Single crystals of **1** and **2** suitable for X-ray structure analysis were grown by slow diffusion of hexane into dichloromethane solutions at 4 °C. Diffraction intensities were collected at 100 K with a Bruker SMART APEX2 CCD diffractometer using Cu Kα radiation (λ = 1.541 78 Å). Indexing and initial cell refinements as well as the data collection were all done using APEX2[26] software. Data integration was accomplished with SAINT[27] software, and numerical absorption correction (based on the real shape of the crystals) followed by a scaling procedure with the SADABS program[28] was used to account for systematic effects. The structures were solved by direct methods[29] and refined by full-matrix least squares.[30] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found in a difference Fourier map and refined isotropically (except those of disordered dichloromethane solvent molecules in structure **1**). Scattering factors were taken from ref 31. Additional details of the data collection and structure refinement are given in Table 1.

Table 1. Crystallographic Data and Structure Refinement Parameters for Compounds 1 and 2

	1	2
empirical formula	C$_{21}$H$_7$N$_1$O$_{14}$Ru$_5$	C$_{39}$H$_{30}$Cl$_3$NO$_6$P$_2$Ru$_3$
fw	1002.63	1080.14
temp (K)	100(2)	100(2)
wavelength (Å)	1.541 78	1.541 78
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	20.5014(4)	11.2693(2)
b (Å)	13.4140(3)	22.9673(4)
c (Å)	20.4567(4)	16.6992(3)
α (deg)	90	90
β (deg)	104.4270(10)	108.6100(10)
γ (deg)	90	90
V (Å^3)	5448.31(19)	4096.18(13)
Z	8	4
calcd density (Mg/m^3)	2.445	1.752
abs coeff (mm^{-1})	22.586	11.767

	1	2
$F(000)$	3776	2128
cryst size (mm^3)	0.27 × 0.12 × 0.12	0.34 × 0.12 × 0.08
θ range for data collecn (deg)	3.98–67.37	3.39–67.24
index ranges	$-24 \leq h \leq 23$	$-13 \leq h \leq 12$
	$0 \leq k \leq 15$	$0 \leq k \leq 27$
	$0 \leq l \leq 24$	$0 \leq l \leq 19$
no. of rflns collected	45 530	34 219
no. of indep rflns	9498 (R(int) = 0.0313)	7111 (R(int) = 0.0268)
max, min transmissn	0.1725, 0.0641	0.4528, 0.1083
no. of data/restraints/params	9498/8/787	7111/3/613
goodness of fit on F^2	1.057	1.055
final R indices ($I > 2\sigma(I)$)	R1 = 0.0244	R1 = 0.0206
	wR2 = 0.0543	wR2 = 0.0476
R indices (all data)	R1 = 0.0285	R1 = 0.0227
	wR2 = 0.0558	wR2 = 0.0485
largest diff peak, hole (e Å^{-3})	1.839, −0.511	0.428, −0.424

Acknowledgment

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