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Ruthenium and Osmium Complexes of Dihydroperimidine-based *N*-Heterocyclic Carbene Pincer Ligands†

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The reactions of *N,N'*-bis(phosphinomethyl)dihydroperimidine pro-ligands $H_2C(NCH_2PR_2)_2C_{10}H_6$ (R = Cy **1a**, R = Ph **1b**) with $[RuCl_2(PPh_3)_3]$ give markedly different products. Chelate-assisted double C–H activation in the former affords the perimidinylidene-based N-heterocyclic carbene (*per*-NHC) pincer complex $[RuCl_2(OC_4H_8)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2**), while the latter reaction provides the asymmetric PNP-coordinated complex $[RuCl_2(PPh_3)\{\kappa^3\text{-}P,N,P'\text{-}CH_2(NCH_2PPh_2)_2C_{10}H_6\}]$ (**3**), in which no C–H activation has occurred. Subsequent reactions of the *per*-NHC complex **2** with carbon monoxide and mesityl isocyanide readily displaced the labile THF ligand to afford the complexes $[RuCl_2(CA)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (A = O **4**, A = $NC_6H_2Me_3$ **5**). Double C–H activation of **1a** and **1b** was significantly more facile on reaction with $[OsCl_2(PPh_3)_3]$, providing the *per*-NHC complexes $[OsHCl(PPh_3)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Cy **7a**, R = Ph **7b**, respectively), each as two isomers. The reactions of **1b** with $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_6H_3Me_3)_2]$ or [AuCl(THT)] (THT = tetrahydrothiophene) provide the bimetallic complexes $[Ru_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_4(\eta\text{-}C_6H_3Me_3)_2]$ (**8**) and $[Au_2\{\mu\text{-}H_2C(NCH_2PPh_2)_2C_{10}H_6\}Cl_2]$ (**9**) without C–H activation occurring.

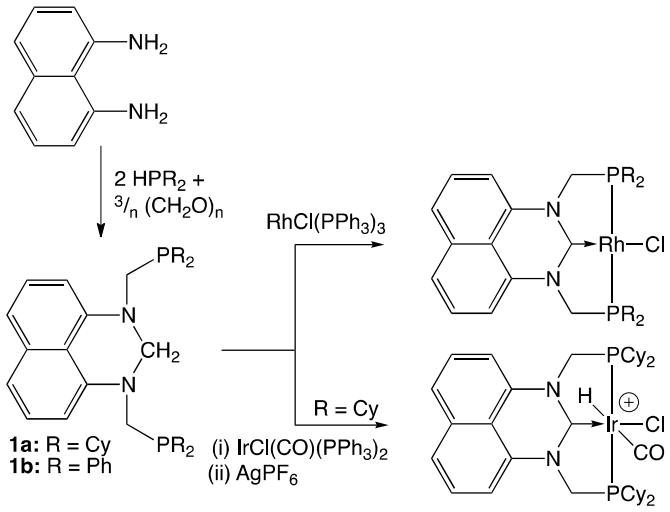
Introduction

N-heterocyclic carbene (NHC) ligands are well established as effective spectator ligands, and as such have become important tools in organometallic chemistry, particularly as ancillaries in catalyst design.[1] Though often compared to tertiary phosphines, NHCs have become attractive alternatives to phosphines due to properties such as increased σ-donating abilities[2] and reduced tendency toward dissociation.[3] One drawback, however, is that free NHCs are generally less readily accessible. A number of strategies for coordinating NHCs to metal centres have therefore been developed, most commonly involving activation of cationic azolium precursors.[4]

Although metal–NHC bonds are inherently strong, they are not necessarily inert, and decomposition via a variety of pathways has been observed.[5] Enhanced NHC stability is hence one among many advantages to be derived from their inclusion within pincer scaffolds. NHCs have been incorporated into these systems both as side-arm donors, and in the central equatorial position.[6] There has been a significant amount of effort directed towards the study of E(NHC)E-type (E = donor arms) pincer complexes over the last two decades, and literature examples incorporate metals from almost all the groups 4 to 11, with group 10 chemistry being the most extensively developed. There are fewer examples of group 8 complexes, most being based on ruthenium,[7] though an iron E(NHC)E pincer complex has also recently been reported.[8] Osmium NHC pincer complexes are however comparatively rare,[9] and to date there do not appear to be any literature examples of such complexes incorporating an E(NHC)E ligand.

We have previously described a number of systems in which a perimidinylidene-based NHC (*per*-NHC) group is incorporated as the central donor of a pincer ligand.[7a,10] These complexes have been prepared from the readily accessible 2,3-dihydroperimidine pro-ligands $H_2C(NC_2PR_2)_2C_{10}H_6$-1,8 (R = Cy **1a**, R = Ph **1b**; Scheme 1). Metallation of these pro-ligands to form NHC complexes proceeded via an unusual method in which they underwent chelate-assisted double geminal aminal C–H bond activation upon direct reaction with rhodium(I) and iridium(I)[10] complexes under remarkably mild conditions (Scheme 1). The direct reactions of pro-ligands **1a** and **1b** with various ruthenium complexes have been briefly communicated,[7a] and in one case also resulted in double

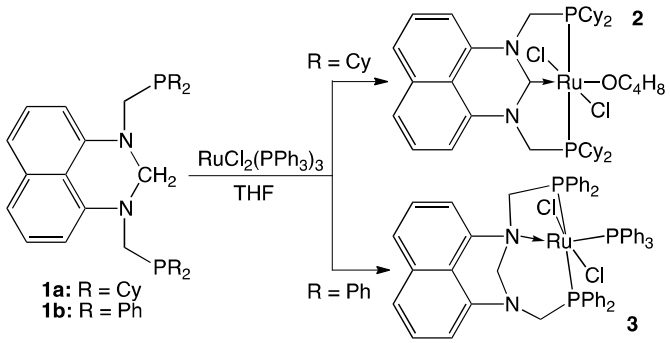
geminal C–H activation to give the *per*-NHC complex $[RuCl_2(OC_4H_8)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2**, *vide infra*). Herein we discuss further investigations into the reactivity of complex **2**, as well as the extension of the NHC-installation methodology to afford the first examples of osmium E(NHC)E pincer complexes.



Scheme 1 Preparation of 2,3-dihydroperimidine pro-ligands and their reactions to form *per*-NHC pincer complexes.[10]

Results and discussion

The reactions of **1a** with $[RuCl_2(PPh_3)_3]$ in tetrahydrofuran resulted in the double geminal C–H bond activation with loss of H_2, to give the *per*-NHC complex $[RuCl_2(OC_4H_8)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (**2**). In contrast, the reaction of the same complex with **1b** afforded the asymmetric PNP complex $[RuCl_2(PPh_3)\{\kappa^3\text{-}P,N,P'\text{-}CH_2(NCH_2PPh_2)_2C_{10}H_6\}]$ (**3**) without C–H activation occurring (Scheme 2).[7a] We presume that the difference in reactivity is largely due to electronic factors, given that C–H activation was notably more facile for the more electron-rich d^8 rhodium(I) systems,[10] though steric factors presumably also play a role.



Scheme 2. Reactions of dihydroperimidine-based pro-ligands with $[RuCl_2(PPh_3)_3]$.[7a]

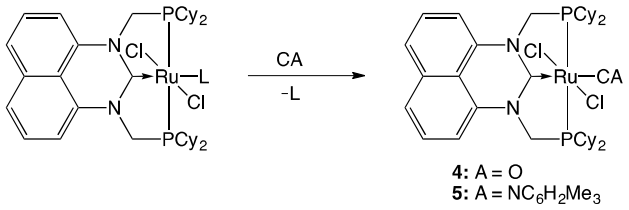
As with other derivatives to follow, it was not always easy to locate the carbene resonance of interest in the $^{13}C\{^1H\}$ NMR spectrum of **2**. In such cases, the resonance was most easily identified from a $^1H^{13}C$ HMBC spectrum which revealed correlation between the carbene ^{13}C resonance (δ_C = 224.7) and that due to the phosphinomethylene groups (at δ_H = 4.26). Complex **2** was found to be very air-sensitive, rapidly changing colour from orange-yellow to green on exposure to air in solution. NMR spectra of the resulting green solution were very broad, similar to those of a minor green side product that was obtained from chromatography of the reaction mixture. This compound (or mixture of compounds) remains unidentified, though the broad spectra suggest paramagnetism due to a ruthenium(III) complex.

It was anticipated that **2** would display interesting reactivity, given that the solvent binding site should be readily available for other substrates, particularly due to its location *trans* to the carbene. However, its formation was accompanied by a significant proportion of side-products, and even after purification by column chromatography and precipitation, NMR data suggested that a small amount of triphenylphosphine remained, and was exchanging with the THF ligand of **2** to give a second complex $[RuCl_2(PPh_3)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$. Analytically pure samples of **2** could only be obtained by small-scale crystallisation. Other attempts involved avoiding PPh_3 in the first place, using $[Ru_2(\mu\text{-}Cl)_2Cl_2(\eta^6\text{-}MeC_6H_4{}^iPr\text{-}4)_2]$ or '$RuCl_3.xH_2O$' as the starting complexes. The reactions of **1a** with the former gave mixtures of compounds from which no one product could be isolated (*vide infra*). Heating a slight excess of **1a** with '$RuCl_3.xH_2O$' in methanol resulted in a green reaction mixture that gave several peaks in the $^{31}P\{^1H\}$ NMR spectrum and broad peaks in the ^1H spectrum. This suggests the presence of one or more paramagnetic Ru(III) complexes, indicating that the excess pro-ligand **1a** does not readily reduce the starting material.

Nevertheless, the crude triphenylphosphine-containing sample '**2**' obtained from **1a** and $[RuCl_2(PPh_3)_3]$ serves as an adequate starting material for reactions in which replacement of the THF/PPh_3 ligand is intended. Based on $^{31}P\{^1H\}$ NMR integrals of free triphenylphosphine and product in the mixtures resulting from these reactions, approximately 20% of crude starting material, obtained as described in the Experimental Section consisted of the PPh_3-containing complex. The average molecular weight of the starting material was calculated accordingly to give approximate yields quoted. This displacement was found to occur readily and irreversibly upon treatment of crude **2** with carbon monoxide and mesityl isocyanide to give complexes $[RuCl_2(CA)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PCy_2)_2C_{10}H_6\}]$ (A = O **4**, A = $NC_6H_2Me_3$ **5**, Scheme 3).

Both these reactions proceeded cleanly with triphenylphosphine and THF being the only side products evident in the NMR spectra of the crude reaction mixtures. Stirring crude '**2**' in DCM under a CO atmosphere caused an immediate colour change from orange to yellow, and the emergence of a $^{31}P\{^1H\}$ NMR peak at δ_P = 47.3 indicated complete conversion to the desired product. The carbene carbon resonance was observed in the $^{13}C\{^1H\}$ spectrum at δ_C = 223.8, very close to that of **2** (δ_C = 224.7), while the CO ligand

appeared at δ_C = 205.5 (coupling constants for these apparent triplet resonances could not be resolved). The coordination of the carbonyl ligand was also evident from an infrared CO absorption at 1974 cm^{-1} (CH_2Cl_2). The reaction of crude '**2**' with mesityl isocyanide also resulted in an instant colour change to give a yellow solution. The $^{31}P\{^1H\}$ NMR spectrum of the purified product **5** comprised a singlet peak at δ_P = 45.6. The presence of the isocyanide ligand was supported by an infrared ν_{CN} absorption at 2088 cm^{-1} (CH_2Cl_2), and a $^{13}C\{^1H\}$ NMR resonance at δ_C = 172.8, while the carbene carbon resonance was observed at δ_C = 229.2.



Scheme 3. Reaction of *per*-NHC pincer ruthenium complexes with CO and $CNC_6H_2Me_3$-2,4,6 (L = THF, PPh_3).

The structures of **4** and **5** were both confirmed by crystallographic studies, and their molecular structures are depicted in Figures 1 and 2, respectively.

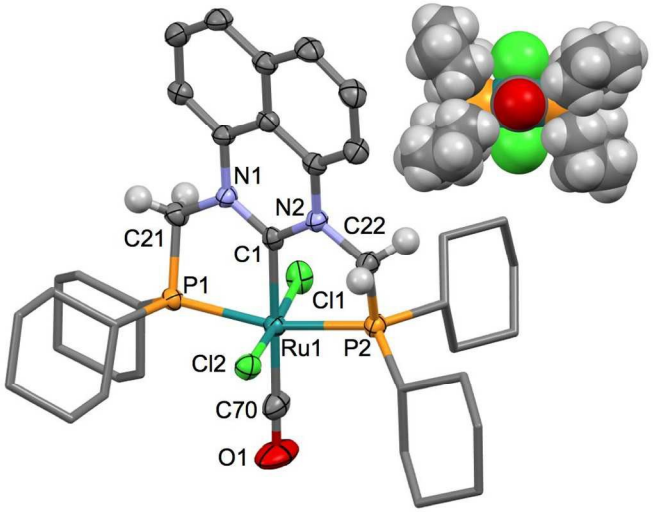


Figure 1. Molecular structure of **4** (aryl and cyclohexyl hydrogen atoms omitted, cyclohexyl groups simplified; 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Ru1–C1 = 2.087(3), Ru1–P1 = 2.3311(8), Ru1–P2 = 2.3249(8), N1–C1 = 1.361(4), N2–C1 = 1.356(4), P1–Ru1–P2 = 163.22(3), P1–Ru1–C1 = 81.41(8). Inset: Space filling representation viewed along the O1-C70 axis

Crystals of the former were obtained from a DCM/*n*-hexane solvent mixture. However, crystals obtained from a $CDCl_3$/*n*-hexane solution of **4** were found instead to be that of the complex salt [RuCl(CO)(PPh_3){κ^3-*P,C,P'*-$C(NCH_2PCy_2)_2C_{10}H_6$}][Cl] ([**6**]Cl) (Figure 3). The presence of the triphenylphosphine ligand in this structure was surprising, given the fact that free triphenylphosphine was liberated in the reaction to form **4** and subsequently presumed to be removed by washing with *n*-hexane, and suggested that perhaps triphenylphosphine ligand exchange may again be a problem with this product, as with **2**. However, when the remaining $CDCl_3$/*n*-hexane crystal sample was redissolved in an NMR sample, only a single peak was observed in the $^{31}P\{^1H\}$ NMR spectrum, consistent with complex **4** and not $\mathbf{6}^+$. Furthermore, variable temperature NMR studies showed no evidence of triphenylphosphine exchange, though this does not necessarily preclude a dynamic process that is very rapid on the NMR time scale.

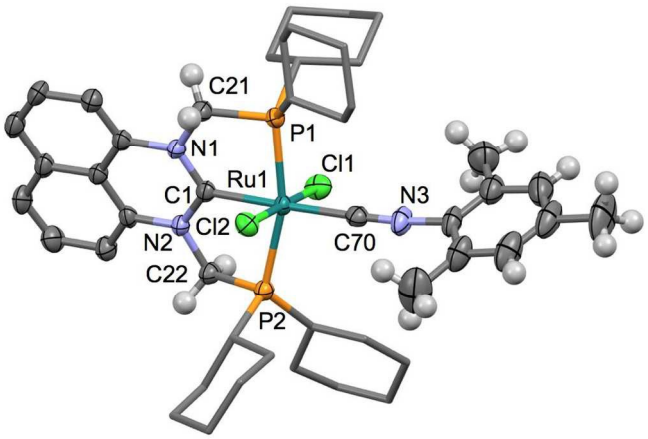


Figure 2. Molecular structure of **5** in a crystal of **5**.$(C_6H_{14})_{0.5}$ (aryl, cyclohexyl and methyl hydrogen atoms omitted, 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg.): Ru1–C1 = 2.052(3), Ru1–P1 = 2.3080(9), Ru1–P2 = 2.3164(9), N1–C1 = 1.365(4), N2–C1 = 1.366(4), P1–Ru1–P2 = 163.44(3), P1–Ru1–C1 = 82.1(1).

The structures of complexes **4**, **5** and $\mathbf{6}^+$ display respectively Ru–C1 bond lengths of 2.087(3) Å, 2.052(3) Å and 2.102(5) Å, each of which is markedly longer than the distance of 1.943(2) Å observed for **2**, presumably due to the stronger *trans*-influence of the CO and CNMes ligands relative to weakly bound THF. All of these values are, however, within the range observed for the copious structural data of NHC complexes of ruthenium(II).[11] The P–Ru–P bond angles show considerable deviations from 180°, to accommodate the geometric constraints of meridional pincer coordination. This angle is particularly contracted in complex $\mathbf{6}^+$, presumably due to interactions of the dicyclohexylphosphino groups with the sterically imposing triphenylphosphine ligand. The dihydroperimidinylidene ring systems exhibit twist angles relative to the C1–P1–P2–C70 coordination planes of 19.9°, 21.8° and 27.5° for complexes **4**, **5** and $\mathbf{6}^+$, respectively. The π-acidity of NHC ligands is generally held to be negligible, such that loss of Ru=C multiple bonding during carbene rotation is not an issue. The more substantial twist in the latter is presumably a further result of steric interactions between the substituents on the *cis*-disposed phosphines. In the former two complexes the twisting is noticeably less pronounced than in **2**, which displayed a twist angle of 29.4°, and this may arise in order to accommodate the relatively short Ru–C1 distance in **2**.

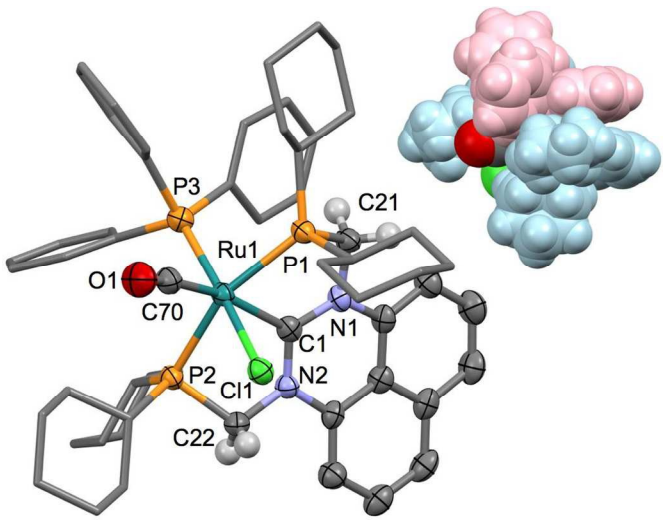
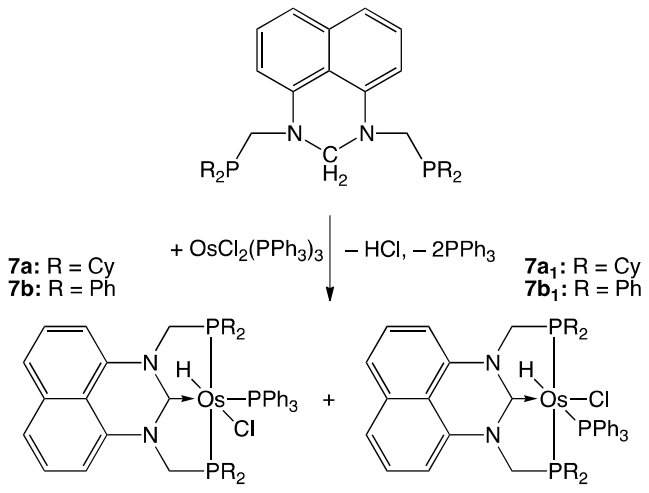


Figure 3. Molecular structure of $[\mathbf{6}]^+$ in a crystal of $[\mathbf{6}]Cl.(CHCl_3)_2$ (chloride counter-anion, solvent aryl and cyclohexyl hydrogen atoms omitted, phosphine substituents simplified, 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Ru1–C1 = 2.102(5), Ru1–P1 = 2.391(1), Ru1–P2 = 2.387(1) , N1–C1 = 1.360(6), N2–C1 = 1.361(6), P1–Ru1–P2 = 159.02(5), P1–Ru1–C1 = 79.8(1). Inset: Steric clash associated with accommodating the bulky PPh_3 (pink) and *per*-NHC ligands (blue).

Given the marked difference between the reactions of **1a** and **1b** with $[RuCl_2(PPh_3)_3]$ the analogous reactions with $[OsCl_2(PPh_3)_3]$ were investigated. The reactions of both **1a** and **1b** proceeded within 30 minutes at room temperature, considerably more rapidly than the analogous reactions with ruthenium (48 hours). Furthermore, double C–H activation was observed in both cases, presumably promoted by the increased basicity of the osmium centre, to give the complexes $[OsHCl(PPh_3)\{\kappa^3\text{-}P,C,P'\text{-}C(NCH_2PR_2)_2C_{10}H_6\}]$ (R = Cy **7a**, R = Ph **7b**; Scheme 4). These provide rare examples of osmium pincer PCP pincer complexes[9] and the only cases that involve an equatorial NHC donor.



Scheme 4. Reactions of dihydroperimidine-based pro-ligands with $[OsCl_2(PPh_3)_3]$.

As in the synthesis of complex **2**, however, attempted purification by column chromatography yielded products that appeared to be mixtures of at least two compounds by ^{31}P and ^{1}H NMR spectroscopy. A spectroscopically pure sample of **7b** could be obtained by fractional crystallisation. However, a mixture of two compounds was still observed in the NMR spectra of the crystals of **7a**. It was thus speculated that the products formed two distinct isomers in solution. This is consistent with the NMR data for the product mixtures, which in both cases displayed two distinct hydride resonances in the ^{1}H spectra and four resonances in the ^{31}P NMR spectra, as summarized in Table 1.

Table 1. Selected NMR chemical shifts and related coupling constants for **7a,b** and isomers.

Complex	δ_{OsH} (ppm)	δ_P (ppm)	$^2J_{PH}$ Hz	$^2J_{PP}$ Hz
7a[a]	–18.61 (dt)	3.2 (t), 15.9 (d)	16, 16	17
7a$_1$[a]	–6.82 (dt)	–10.8 (m), 1.2 (d)	88, 26	11
7b[b]	–18.46 (dt)	5.2 (m), 11.8 (d)	17, 17	18
7b$_1$[a]	–6.23 (dt)	–3.9 (t), 0.1 (d)	85, 25	13

[a] C_6D_6; [b] $CDCl_3$

It was determined that the higher field hydride shifts at *ca* δ_H = –18.5 correspond to the complexes **7a,b** that were obtained in crystal form (*vide infra*), as well as the two downfield ^{31}P NMR resonances. The hydride and ^{31}P resonances of the other complexes in each mixture, **7a$_1$** and **7b$_1$**, display the same multiplicities as those of **7a** and **7b**. For **7a,b**, the doublet of triplet hydride resonance appears as a quartet due to identical *cis*-J_{PH} values for the PPh_3 and PPh_2 groups. Both complexes **7a$_1$** and **7b$_1$** also give a doublet of triplet hydride resonance, though in these cases one of the J_{PH} couplings is very large, suggesting that one of the phosphine groups is situated *trans* to the hydride in these complexes. This observation is consistent with isomers of **7a** and **7b** in which the chloride and triphenylphosphine ligands are exchanged, as depicted in Scheme 4. Formation of **7b**, rather than its isomer **7b$_1$**, appeared to be favored in chlorinated solvents. Consequently, **7b** could be isolated cleanly from the reaction (after column chromatography) when DCM was used as a solvent instead of THF. Unfortunately **7a** could not be isolated in a similar manner, and could only be obtained as a mixture with **7a$_1$**.

Figure 4 depicts the molecular structure of **7a**, as well as views along the pincer coordination planes for both **7a** and **7b**. The Os1–C1 distances do not differ significantly between the two complexes. Complex **7b** exhibits a substantial twist angle of 27.0°, which again may be the result of steric interactions between the di- and triphenylphosphine groups. However, in **7a** the plane of the ring system is virtually parallel to the plane occupied by the coordinating atoms of the pincer ligand, due to the internal crystallographic mirror plane (*P*nma symmetry) that includes C1, Cl1, H1 and P3. The twisting of the unique half of the ring system is larger, with an angle of 8.8°.

Furthermore, though there is no significant disorder, the thermal ellipsoids of the atoms in the perimidine ring system in **7a** indicate libration around the axis containing the C1–Os1 vector.

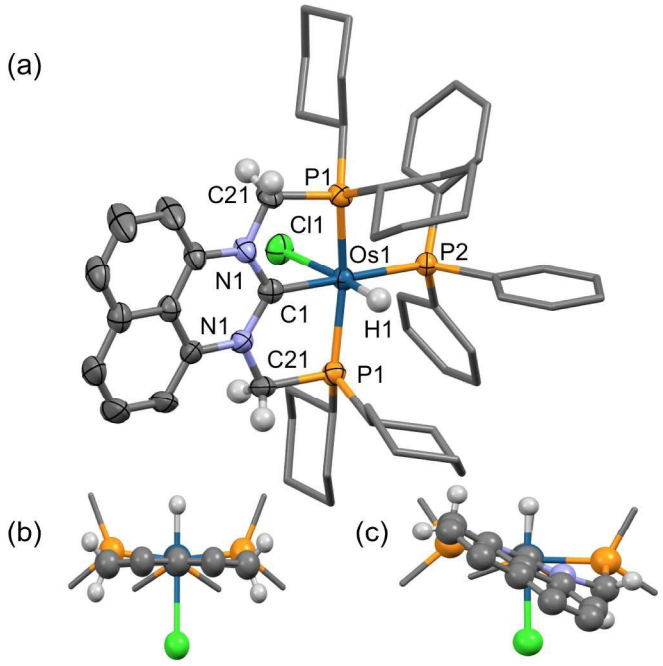
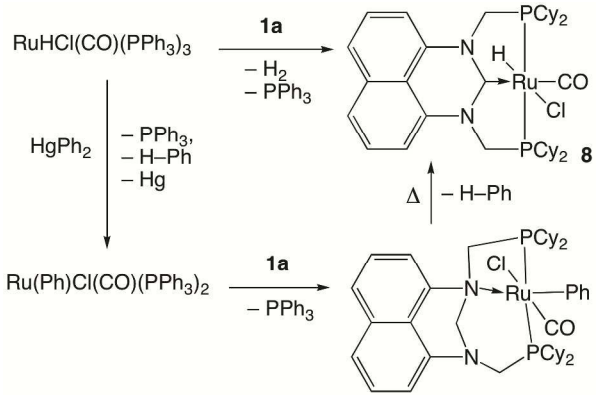


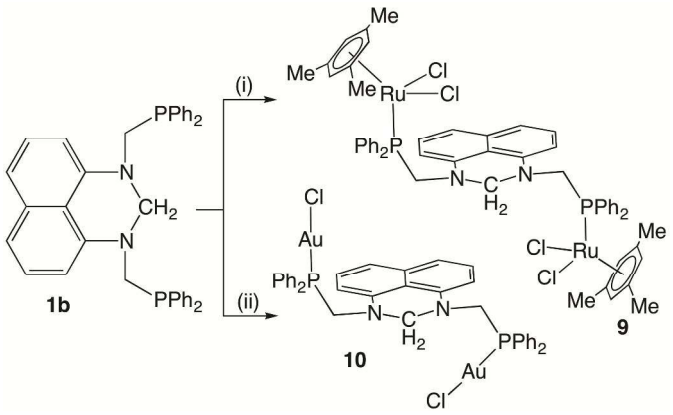
Figure 4. (a) Molecular structure of **7a** in a crystal of **7a**.CH_2Cl_2 (aryl and cyclohexyl hydrogen atoms omitted, phosphine substituents simplified, 50% displacement ellipsoids) and views along the coordination planes of (b) **7a** and (c) **7b**. Selected bond lengths (Å) and angles (deg.) for **7a**: Os1-C1 = 2.051(10), Os1–H1 = 1.70(12), C1–N1 = 1.391(8), P1–C21 = 1.827(8), C1–Os1–P1 = 81.65(6), P1–Os1–P1′ = 159.12(9), C1–Os1–P2 = 179.3(3). (P1^{i} is a symmetry-generated atom equivalent to P2). Selected corresponding bond lengths for **7b**: Os1-C1 = 2.002(12), Os1–H1 = 1.69(9), C1–N1 = 1.385(12), C1–N2 = 1.425(13), P1–C21 = 1.844(41), P2–C22 = 1.839(10), C1–Os1–P1 = 79.1(3), P1–Os1–P2 = 157.69(9), C1–Os1–P3 = 177.9(3).

The corresponding ruthenium complex [RuHCl(CO){κ^3-*P,C,P'*-C(NCH$_2$PR$_2$)$_2$C$_{10}$H$_6$}] (**8**) has been briefly described as resulting from the thermolysis of the PNP pincer complex [Ru(C$_6$H$_5$)Cl(CO){κ^3-*N,P,P'*-H$_2$C(NCH$_2$PCy$_2$)C$_{10}$H$_6$}] via benzene elimination and α-RuH-elimination of the remaining perimidinyl C–H hydrogen to ruthenium to install the hydride ligand (Scheme 5). A more succinct and convenient approach to **8** which affords purer material directly from the reaction mixture involves the reaction of **1a** with *mer*-[RuHCl(CO)(PPh$_3$)$_3$] in refluxing toluene. The product is only sparingly soluble in toluene such that the liberated PPh$_3$ and minor side products remain in the supernatant.

The coordination of **1b** to metal centres for which C–H activation is disfavored was briefly explored. Thus the reaction of [Ru$_2$(μ-Cl)$_2$Cl$_2$(η-C$_6$H$_3$Me$_3$-2,4,6)$_2$] and **1b** in dichloromethane proceeded to completion over a period of 90 minutes as indicated by ^{31}P{^{1}H} NMR spectroscopy, which indicated the development of a single resonance at δ_P –23.6. High resolution ESI mass spectrometry confirmed the formation of the bimetallic product [Ru$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_4$(η-C$_6$H$_3$Me$_3$-2,4,6)$_2$] **9** that was obtained in reasonable yield (78%, Scheme 6).



Scheme 5. Alternative routes to [RuHCl(CO){=C(NCH$_2$PR$_2$)$_2$C$_{10}$H$_6$}] (**8**).



Scheme 6. Synthesis of Homobimetallic Complexes (i) [Ru$_2$Cl$_4$(C$_6$H$_3$Me$_3$)$_2$]; (ii) [AuCl(THT)].

In contrast to the reaction of **1b** with [Ru$_2$(μ-Cl)$_2$Cl$_2$(η^6-MeC$_6$H$_4$^{i}Pr)$_2$] discussed above, which lead to a number of unidentified products, a solution of **9** in dichloromethane showed no change over a period of 20 hours, and no indication of C–H activation. This may most likely be attributed to the stronger bonding of mesitylene to the ruthenium centre than the more labile p-cymene. The characterisation of **9** included a crystallographic analysis (Figure 5), which confirmed the binuclear nature and that upon coordination, **1b** remained intact. There is no direct interaction between the two ruthenium centres which are separated by *ca* 10 Å. A very closely related analogue of **9**, [Ru$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_4$(η-C$_6$H$_6$)$_2$] has recently been reported.[12]

In a similar manner, the reaction of **1b** with [AuCl(THT)] (THT = tetrahydrothiophene) proceeded over 20 hours at room temperature to afford [Au$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}Cl$_2$] **10**. Losses during purification (colloidal gold formation), however, resulted in a low yield of pure product (25%). The spectroscopic data for **10** are unremarkable other than to confirm the retention of the intact aminal methylene unit. The crystal structure determination of **10** (Figure 6) indicates that

there are not aurophilic interactions between the two gold centres which are located some 7 Å apart.

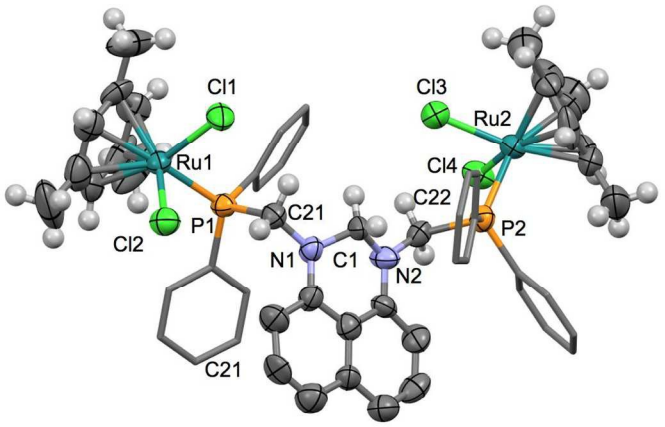


Figure 5. Molecular structure of **9** in a crystal of **9**.$CHCl_3$ (solvent and aryl hydrogen atoms omitted, phenyl groups simplified, 60% displacement ellipsoids, one of two crystallographically independent molecules shown). Selected bond lengths (Å) and angles (deg): Cl1–Ru1 2.416(3), Cl2–Ru1 2.420(4), Cl3–Ru2 2.410(4), Cl4–Ru2 2.404(4), P1–Ru1 2.356(3), P2–Ru2 2.350(4), Ru(1)···Ru(2) 10.133, Ru(3)···Ru(4) 10.105, P1–C21–N1 113.4(9), P2–C22–N2 119.9(9).

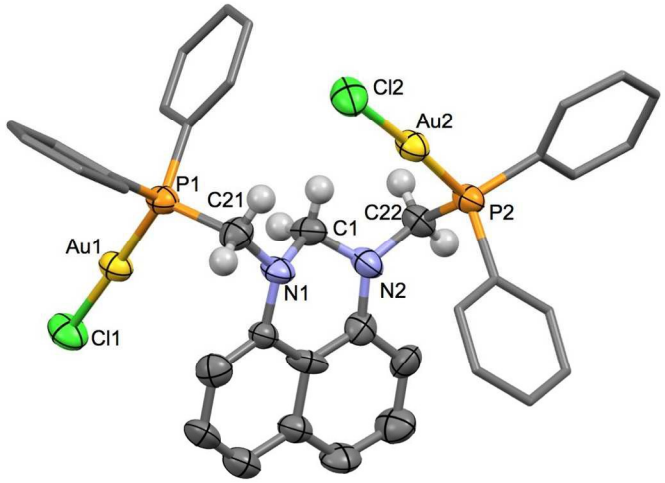
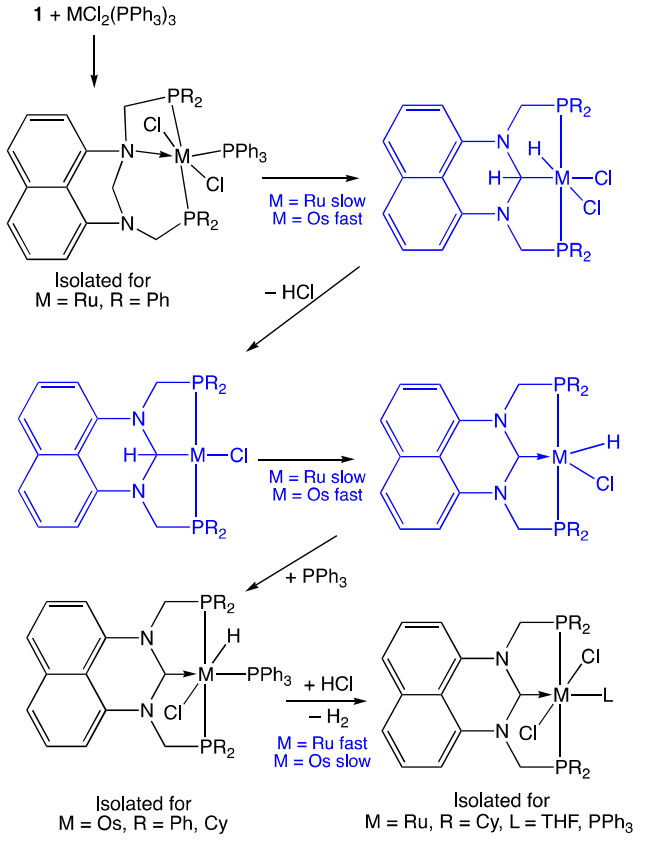


Figure 6. Molecular structure of **10** in a crystal of **10**.$(CHCl_3)_2$ (solvent and aryl hydrogen atoms omitted, phenyl groups simplified, 60% displacement ellipsoids). Selected bond lengths (Å) and angles (deg): Au1–Cl1 2.294(3), Au1–P1 2.231(3), Au2–Cl2 2.291(3), Au2–P2 2.239(3), Au1···Au2 7.038, Cl1–Au1–P1 177.35(11), Cl2–Au2–P2 176.26(10), P1–C21–N1 116.1(8), P2–C22–N2 107.8(7).

Conclusions

The slow reaction of **1a** with $[RuCl_2(PPh_3)_3]$ under mild conditions resulted in double geminal dehydrogenation of the central methylene group to give the NHC pincer complex **2**. However, the analogous reaction of the less electron-donating pro-ligand **1b** with $[RuCl_2(PPh_3)_3]$ gave the asymmetric PNP coordinated complex **3**, in which no C–H activation had occurred. Complex **2** was subsequently observed to react with carbon monoxide or mesityl isocyanide to give complexes **4** and **5**, respectively.

N-heterocyclic carbene pincer complexes of osmium were also generated in direct reactions between the pro-ligands **1a** and **1b** with $[OsCl_2(PPh_3)_3]$ providing the first examples of E(NHC)E pincer complexes of osmium. Generation of the NHC complexes **7a** and **7b** was significantly more facile than in the analogous ruthenium chemistry, reinforcing the observation that carbene formation will occur more readily for electron-rich systems (PCy_2 > PPh_2) and that 5d metals more readily enter into C–H activation processes than do their 4d counterparts (Os > Ru).[13] The isolation of the *mono*-hydrido osmium complexes **7** provides some insight into the likely mechanism of formation of **2** and **3** (Scheme 7), suggesting that a similar complex $[RuHCl(PPh_3)\{C(NCH_2PR_2)_2C_{10}H_6\}]$ (**8**) is the key intermediate rather than either a ruthenium(II) dihydrogen complex $[Ru(H_2)Cl_2\{C(NCH_2PR_2)_2C_{10}H_6\}]$ or ruthenium(IV) dihydride $[RuH_2Cl_2\{C(NCH_2PR_2)_2C_{10}H_6\}]$. Hydrogen chloride liberated during the slow formation of **8** would thus appear to rapidly protolyse the hydride ligand in **8**, but in the case of **7**, the Os–H linkage is more robust, as indicated by its stability in chloroform. The role that liberated PPh_3 plays in such a mechanism, either as a base or in stabilizing coordinatively unsaturated intermediates remains open to conjecture.



Scheme 7. Proposed mechanism for double geminal C–H activation (inferences in blue, isolated compounds in black).

Experimental Section

General Considerations. All manipulations of air-sensitive compounds were carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk and vacuum line techniques, with dry and degassed solvents. NMR spectra were recorded at 25°C on Varian Mercury 300 (^{1}H at 300.1 MHz, ^{31}P at 121.5 MHz), Inova 300 (^{1}H at 299.9 MHz, ^{13}C at 75.42 MHz, ^{31}P at 121.4 MHz), Inova 500 (^{1}H at 500.0 MHz, ^{13}C at 125.7 MHz) or MR 400 (^{1}H at 399.9 MHz, ^{31}P at 161.9 MHz) spectrometers. The chemical shifts (δ) for ^{1}H and ^{13}C spectra are given in ppm relative to residual signals of the solvent and ^{31}P relative to an external H_3PO_4 reference. Virtual triplet resonances are indicated by t^v. Low and high resolution mass spectra were obtained on a ZAB-SEQ4F spectrometer by +ve ion ESI techniques using an acetonitrile matrix by the mass spectrometry service of the Australian National University. Assignments were made relative to M, where M is the molecular cation. Assignments were verified by simulation of isotopic composition both for low and high resolution levels. Elemental microanalysis was performed by the microanalytical service of the Australian National University. Data for X-ray crystallography were collected with Nonius Kappa CCD or Agilent SuperNova diffractometers. The compounds **1a** and **1b**[10] were prepared according to published procedures. Other reagents were used as received from commercial suppliers.

Synthesis of [RuCl$_2$(THF){C(NCH$_2$PCy$_2$)$_2$C$_{10}$H$_6$}] (2). A solution of [RuCl$_2$(PPh$_3$)$_3$] (0.200 g, 0.209 mmol) and **1a** (0.123 g, 0.208 mmol) in THF (20 mL) was stirred for 48 hrs. The solution was freed of volatiles under reduced pressure. The residue was redissolved in THF and chromatographed on silica gel using a 20% mixture of THF in *n*-hexane as eluent. An orange band was collected and the solvent removed under reduced pressure. The residue was redissolved in toluene and *n*-hexane added, followed by storage at –18°C to afford the crude product as a yellow precipitate. This was separated from the supernatant via cannula filtration. X-ray quality crystals and analytically pure samples of **2** were obtained by slow diffusion of *n*-hexane into a THF solution of the product. Yield (crude): 0.068 g (39%). IR (KBr, cm^{-1}): 3052 ν_{aromCH}; 2963, 2921, 2848 ν_{CH}; 1579 ν_{aromCC}. NMR (CDCl$_3$, 298 K) ^{1}H: δ_H = 1.26-1.91 (set of multiplets, 48 H, C$_6$H$_{11}$ and CH$_2$(THF)), 2.64 (br, 4 H, OCH$_2$(THF)), 4.24 (br, 4 H, PCH$_2$), 6.71 (d, 2 H, C$_{10}$H$_6$, $^3J_{HH}$ = 8 Hz), 7.31-7.38 (m, 4 H, C$_{10}$H$_6$). ^{13}C{^{1}H}: δ_C = 26.2 (C$_6$H$_{11}$), 27.4 (t^v, C$_6$H$_{11}$, J_{PC} = 5), 27.7 (t^v, C$_6$H$_{11}$, J_{PC} = 6), 28.7, 28.9 (C$_6$H$_{11}$), 34.6 (t^v, C$_6$H$_{11}$, J_{PC} = 10), 34.9, 37.3 (C$_6$H$_{11}$ or C$_4$H$_8$O), 52.3 (t^v, PCH$_2$, J_{PC} = 14 Hz), 105.3, 118.7, 120.5, 128.1, 134.4, 134.9 (C$_{10}$H$_6$)). HMBC: $\delta_C(\delta_H)$ = 224.7(4.24) (Ru=CN$_2$). ^{31}P{^{1}H}: δ_P = 34.6. ESI-MS (+ve ion, MeCN): *m/z* = 725.6 [M – THF – Cl]$^+$. Anal. Found: C, 60.03; H, 8.44;[14] N, 3.06%. Calcd. for C$_{45}$H$_{70}$Cl$_2$N$_2$O$_2$P$_2$Ru: C, 59.72; H, 7.80; N, 3.10%. *Crystal data for* C$_{41}$H$_{62}$Cl$_2$N$_2$OP$_2$Ru: M_r = 832.88, monoclinic, *C*2/*c*, *a* = 24.8338(2), *b* = 15.2417(1), *c* = 23.7802(2) Å, *β* =90.5012(5)°, *V* = 9000.7(1) Å^3, *Z* = 8, D_{calcd} = 1.229 Mg m^{-3}, μ(Mo Kα) = 0.57 mm^{-1}, *T* = 200(2) K, orange block, 0.26 x 0.19 x 0.17 mm, 10316 independent reflections. F^2 refinement, R_1 = 0.034, wR_2 = 0.084 for 8765 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 497 parameters, CCDC 983020.

Synthesis of [RuCl$_2$(PPh$_3$){CH$_2$(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_6$}] (3). A solution of [RuCl$_2$(PPh$_3$)$_3$] (0.200 g, 0.209 mmol) and **1b** (0.118 g, 0.208 mmol) in THF (20 mL) was stirred for 18 hrs. The solution was freed of volatiles under reduced pressure, and ethanol (12 mL) added to the residue. The suspension was stirred for 64 hrs and the pinkish-brown solid product separated from the supernatant via cannula filtration. X-ray quality crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the product. Yield: 0.142 g (68%). IR (KBr, cm^{-1}): 3049 ν_{aromCH}; 1597, 1584, 1482, 1433 ν_{aromCC}. NMR (CDCl$_3$, 298 K) ^{1}H: δ_H = 4.16, 4.18 (d x 2, 1 H x 2, N$_2$CH$_2$, $^2J_{HH}$ = 4 Hz), 4.83, 5.48 (d x 2, 2 H x 2, PCH$_2$, $^2J_{HH}$ = 14), 6.26 (d, 2 H, C$_{10}$H$_6$, $^3J_{HH}$ = 11), 6.37 (d, 2 H, C$_{10}$H$_6$, $^3J_{HH}$ = 8 Hz), 6.76-7.87 (set of multiplets, 37 H, C$_6$H$_5$ and C$_{10}$H$_6$). ^{13}C{^{1}H}: δ_C = 64.2 (br, PCH$_2$), 73.5 (N$_2$CH$_2$), 116.2, 120.3, 122.3, 125.2 (C$_{10}$H$_6$), 126.7 [d, C^{2,6}(C$_6$H$_5$), $^2J_{PC}$ = 10 Hz], 127.2 [t^v, C^{2,6}(C$_6$H$_5$), J_{PC} = 4 Hz], 127.5 [t^v, C^{2,6}(C$_6$H$_5$), J_{PC} = 5 Hz], 128.6 [d, C^1(C$_6$H$_5$), $^1J_{PC}$ = 28 Hz], 134.1 (C$_{10}$H$_6$), 134.5 [t^v, C^{3,5}(C$_6$H$_5$), J_{PC} = 5], 134.9 [d, C^{3,5}(C$_6$H$_5$), $^3J_{PC}$ = 9 Hz], 136.3 [t^v, C^4(C$_6$H$_5$), J_{PC} = 5 Hz], 143.6 (C$_{10}$H$_6$). ^{31}P{^{1}H}: δ_P = –16.9 (br, PPh$_2$), 55.1 (t, PPh$_3$, $^2J_{PP}$ = 29 Hz). NMR (toluene-d$_8$, 198 K) ^{31}P{^{1}H}: δ_P = –26.0 (dd, PPh$_2$, $^2J_{PP}$ = 292, 28), –9.0 (dd, PPh$_2$, $^2J_{PP}$ = 293, 28), 57.3 (t, PPh$_3$, $^2J_{PP}$ = 28 Hz). For VT-^{31}P NMR and ^{1}H^{1}H COSY spectra see Supporting information reference 7a. ESI-MS (+ve Ion, MeCN): *m/z* = 1006.6 [M – Cl + MeCN]$^+$, 929.6 [M – Cl –HCl]$^+$, 667.4 [M – PPh$_3$ – Cl – HCl]$^+$. Accurate Mass: Found 1006.1954 [M – Cl + MeCN]$^+$, Calcd. for C$_{57}$H$_{50}$^{35}Cl ^{14}N$_3$^{31}P$_3$^{102}Ru 1006.1950. Anal. Found: C, 65.95; H, 4.78; N, 2.62%. Calcd. for C$_{55}$H$_{47}$Cl$_2$N$_2$P$_3$Ru: C, 66.00; H, 4.73; N, 2.80%. *Crystal data for* C$_{55}$H$_{47}$Cl$_2$N$_2$P$_3$Ru.CH$_2$Cl$_2$: M_r = 1085.82, triclinic, *P*–1 (no. 2), *a* = 11.3781(2), *b* = 12.6054(4), *c* = 18.8891(6) Å, *α* = 71.390(1), *β* = 76.443(2)°, *γ* = 72.423(2)°, *V* = 2418.9(1) Å^3, *Z* = 2, D_{calcd} = 1.491 Mg m^{-3}, μ(Mo Kα) = 0.69 mm^{-1}, *T* = 200(2) K, orange needle, 0.28 x 0.10 x 0.04 mm, 11119 independent reflections. F^2 refinement, R_1 = 0.042, wR_2 = 0.085 for 7968 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 605 parameters, CCDC 983019.

Synthesis of [RuCl$_2$(CO){C(NCH$_2$PCy$_2$)$_2$C$_{10}$H$_6$}] (4). The crude mixture of '**2**' obtained above (containing PPh$_3$ and **2**, 0.061 g, *ca* 0.071 mmol) was dissolved in dichoromethane (2 mL), and the solution frozen using liquid nitrogen. The atmosphere in the flask was evacuated and replaced with carbon monoxide (three times). The flask was allowed to warm to ambient temperature, causing the orange solution to become pale yellow and some precipitate to form. The solvent was removed under reduced pressure and NMR data showed 100% conversion to the desired product. The residue was washed with *n*-hexane and then dried *in vacuo*. X-ray quality crystals were obtained by slow diffusion of *n*-hexane into a DCM solution of the product. Yield: 0.046 g (*ca* 82%). IR (KBr, cm^{-1}): 2927, 2851 ν_{CH}; 1978 ν_{CO}; 1584 ν_{aromCC}. IR (CH$_2$Cl$_2$, cm^{-1}): 1974 ν_{CO}. NMR (CDCl$_3$, 298 K) ^{1}H: δ_H = 1.27-2.05 (set of multiplets, 40 H, C$_6$H$_{11}$), 2.59 (m, 4 H, C$_6$H$_{11}$), 4.54 (br, 4 H, PCH$_2$N), 6.83

(dd, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2 Hz), 7.36-7.43 (set of multiplets, 4 H, $C_{10}H_6$). $^{13}C\{^1H\}$: δ_C = 26.1 (C_6H_{11}), 27.3 (t^v, C_6H_{11}, J_{PC} = 6), 27.7 (t^v, C_6H_{11}, J_{PC} = 6), 28.9, 29.2, 31.7 (C_6H_{11}), 34.3 (t^v, C_6H_{11}, J_{PC} = 11), 54.7 (t^v, PCH_2, J_{PC} = 14 Hz), 106.9, 120.4, 121.8, 128.2, 134.3, 134.6 ($C_{10}H_6$,), 205.5 (CO, $^2J_{PC}$ apparent but not resolved), 223.8 (Ru=CN_2, $^2J_{PC}$ apparent but not resolved). $^{31}P\{^1H\}$: δ_P = 47.3. ESI-MS (+ve ion, MeCN): *m/z* = 794.6 $[M - Cl + MeCN]^+$, 752.8 $[M - Cl]^+$, 718.8 $[M - Cl - HCl]^+$. Accurate Mass: Found 794.2710 [M – Cl + MeCN], Calcd. for $C_{40}H_{57}{}^{35}Cl^{14}N_3{}^{16}O^{31}P_2{}^{102}Ru$ 794.2709. Anal. Found: C, 55.29; H, 6.90; N, 3.55%. Calcd. for $C_{38}H_{54}Cl_2N_2OP_2Ru.0.5(CH_2Cl_2)$: C, 55.63; H, 6.67; N, 3.37% (The presence of DCM was confirmed by ^1H NMR integration and by crystallography. This was excluded from the crystal structure model using Platon Squeeze due to a high degree of positional disorder). *Crystal data for* $C_{38}H_{54}Cl_2N_2OP_2Ru$: M_r = 788.78, triclinic, *P*–1 (no. 2), *a* = 12.3266 (3), *b* = 13.0965(4), *c* = 13.1070(2) Å, α = 101.840(2), β = 101.575(2), γ = 95.326(1)°, *V* = 2008.89(9) Å^3, *Z* = 2, $D_{calcd.}$ = 1.304 Mg m^{-3}, μ(Mo Kα) = 0.63 mm^{-1}, *T* = 200(2) K, yellow block, 0.21 x 0.18 x 0.12 mm, 9180 independent reflections. F^2 refinement, R_1 = 0.043, wR_2 = 0.107 for 6886 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 415 parameters, CCDC 996764.

Slow diffusion of *n*-hexane into a $CDCl_3$ solution of the product yielded a small number of X-ray quality crystals of the compound $[RuCl(CO)(PPh_3)\{C(NCH_2PCy_2)_2C_{10}H_6\}][Cl]$ ([**6**]Cl) as a bis(chloroform) solvate which was not detected in the bulk sample by NMR spectroscopy, nor further pursued preparatively. *Crystal data for* $C_{56}H_{69}ClN_2OP_3Ru.Cl(CHCl_3)_2$: M_r = 1289.83, monoclinic, $P2_1/c$, *a* = 21.3372(3), *b* = 10.7621(1), *c* = 29.9142(5) Å, β = 93.0438(7)°, *V* = 6859.6(2) Å^3, *Z* = 4, D_{calcd} = 1.249 Mg m^{-3}, μ(Mo Kα) = 0.65 mm^{-1}, *T* = 200(2) K, pale yellow lath, 0.26 x 0.10 x 0.03 mm, 12019 independent reflections. F^2 refinement, R_1 = 0.064, wR_2 = 0.131 for 9139 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 50°), 658 parameters, CCDC 996763.

Synthesis of $[RuCl_2(CNC_6H_2Me_3)\{C(NCH_2PCy_2)_2$-$C_{10}H_6\}]$ (5). The crude mixture of '**2**' obtained above (containing PPh_3 and **2**, 0.092 g, *ca* 0.11 mmol) was dissolved in THF (5 mL) and mesityl isocyanide (0.032 g, 0.22 mmol) added with stirring. The orange solution instantly became dark yellow. The solvent was removed under reduced pressure, and NMR data showed 100% conversion to the desired product. The residue was recrystallised from a mixture of dichloromethane and *n*-hexane. X-ray quality crystals were obtained by slow diffusion of *n*-hexane into a chloroform solution of the product. Yield: 0.074 g (*ca* 76%). IR (KBr, cm^{-1}): 2924, 2850 ν_{CH}; 2085, 2042 $\nu_{C\equiv N}$; 1582 ν_{aromCC}. IR (DCM, cm^{-1}): 2088 $\nu_{C\equiv N}$. NMR ($CDCl_3$, 298 K) ^1H: δ_H = 1.23-2.10 (set of multiplets, 40 H, C_6H_{11}), 2.29 (s, 3 H, *p*-$MesCH_3$), 2.47 (s, 6 H, *o*-$MesCH_3$), 2.62 (br, 4 H, C_6H_{11}), 4.50 (s, 4 H, PCH_2N), 6.80 (dd, 2H, $C_{10}H_6$, $^3J_{HH}$ = 6, $^4J_{HH}$ = 2 Hz), 6.91 (s, 2 H, C_6H_2), 7.35 (m, 4 H, $C_{10}H_6$). $^{13}C\{^1H\}$: δ_C = 19.0 (*o*-$MesCH_3$), 21.3 (*p*-$MesCH_3$), 26.2 (C_6H_{11}), 27.4 (t^v, C_6H_{11}, J_{PC} = 6), 27.7 (t^v, C_6H_{11}, J_{PC} = 6), 28.9, 29.2 (C_6H_{11}), 34.6 (t^v, C_6H_{11}, J_{PC} = 11), 54.8 (t^v, PCH_2, J_{PC} = 14), 106.3, 119.9, 120.8, 126.8, 128.0, 128.4 ($C_{10}H_6$), 134.1, 134.5, 134.7, 136.6 (C_4H_2), 172.8 (t, RuC≡N, $^2J_{PC}$ = 12), 229.2 (t, Ru=CN_2, $^2J_{PC}$ = 8 Hz). $^{31}P\{^1H\}$: δ_P = 45.6. ESI-MS (+ve ion, MeCN): *m/z* = 911.7 $[M - Cl + MeCN]^+$, 870.7 $[M - Cl]^+$. Accurate Mass: Found 911.3657 [M – Cl + MeCN], Calcd. for $C_{49}H_{68}{}^{35}Cl^{14}N_4{}^{31}P_2{}^{102}Ru$ 911.3651. Anal. Found: C, 62.59; H, 7.40; N, 4.84%. Calcd. for $C_{47}H_{65}Cl_2N_3P_2Ru$: C, 62.31; H, 7.23; N, 4.64%. *Crystal data for* $C_{47}H_{65}Cl_2N_3P_2Ru.0.5(C_6H_{14})$: M_r = 949.06, triclinic, *P*–1 (no. 2), *a* = 12.1895(3), *b* = 13.3031(4), *c* = 17.2277(6) Å, α = 104.641(2)°, β = 105.887(2)°, γ = 103.368(2)°, *V* = 2460.5(1) Å^3, *Z* = 2, D_{calcd} = 1.281 Mg m^{-3}, μ(Mo Kα) = 0.53 mm^{-1}, *T* = 200(2) K, yellow lath, 0.17 x 0.08 x 0.03 mm, 11695 independent reflections. F^2 refinement, R_1 = 0.062, wR_2 = 0.107 for 8763 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 56°), 523 parameters, CCDC 996765.

Synthesis of $[OsHCl(PPh_3)\{C(NCH_2PCy_2)_2C_{10}H_6\}]$ (7a/7a$_1$). A mixture of $[OsCl_2(PPh_3)_3]$ (0.150 g, 0.143 mmol) and **1a** (0.085 g, 0.14 mmol) in benzene (15 mL) was stirred for 30 min. The yellow-brown mixture was filtered via cannula, and the filtrate freed of volatiles under reduced pressure. The residue was chromatographed on silica gel initially using benzene to elute undesired side products, followed by THF to elute a broad yellow band, which was freed of volatiles to afford the product as a yellow powder. All NMR spectra of the product showed peaks for two different species (**7a**/**7a$_1$**), which was deemed to be due to isomerisation in solution. X-ray quality crystals of **7a**.CH_2Cl_2 were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the product. Yield (both isomers): 0.088 g (57%). NMR (C_6D_6, 298 K) ^1H: δ_H = –18.61 (dt, 1 H, OsH(**7a**), $^2J_{PH}$ = 16, $^2J_{PH}$ = 16), –6.82 (dt, 1 H, OsH(**7a$_1$**), $^2J_{PH}$ = 88, $^2J_{PH}$ = 26), 1.12-2.89 (series of multiplets, C_6H_{11}), 3.18 (d, 2 H, PCH_2(**7a$_1$**), $^2J_{HH}$ = 13), 3.79 (d, 2 H, PCH_2(**7a$_1$**), $^2J_{HH}$ = 13), 3.87 (d, 2 H, PCH_2(**7a**), $^2J_{HH}$ = 12), 4.54 (d, 2 H, PCH_2(**7a**), $^2J_{HH}$ = 13), 6.18 (d, 2 H, $C_{10}H_6$(**7a$_1$**), $^3J_{HH}$ = 8), 6.61 (d, 2 H, $C_{10}H_6$(**7a**), $^3J_{HH}$ = 7 Hz), 6.73-8.28, (series of multiplets, $C_{10}H_6$ and C_6H_5). $^{31}P\{^1H\}$: δ_P = –10.8 (m, PPh_3(**7a$_1$**)), 1.2 (d, PCy_2(**7a$_1$**), $^2J_{PP}$ = 11), 3.2 (t, PPh_3(**7a**), $^2J_{PP}$ = 17), 15.9 (d, PCy_2(**7a**), $^2J_{PP}$ = 17 Hz). ESI-MS (+ve ion, MeCN): *m/z* = 1084.5 $[M - Cl + MeCN]^+$, 1043.4 $[M - Cl]^+$. Accurate Mass: Found: 1043.4390 $[M - Cl]^+$, Calcd. for $C_{55}H_{70}{}^{14}N_2{}^{192}Os^{31}P_3$ 1043.4367. Anal. Found:[14] C, 61.98; H, 6.10; N, 2.44%. Calcd. for: $C_{55}H_{70}ClN_2OsP_3$, 61.30; H, 6.55; N, 2.60%. *Crystal data for* $C_{55}H_{70}ClN_2OsP_3.CH_2Cl_2$: M_r = 1162.68, orthorhombic, *Pnma*, *a* = 20.2271(3), *b* = 19.8350(2), *c* = 14.1997(2) Å, *V* = 2410.1(4) Å^3, *Z* = 4, $D_{calcd.}$ = 1.355 Mg m^{-3}, μ(Mo Kα) = 2.50 mm^{-1}, *T* = 200(2) K, yellow prism, 0.22 x 0.09 x 0.08 mm, 6711 independent reflections. F^2 refinement, R_1 = 0.058, wR_2 = 0.150 for 5499 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 55°), 341 parameters, CCDC 996761.

Synthesis of $[OsHCl(PPh_3)\{C(NCH_2PPh_2)_2C_{10}H_6\}]$ (7b/7b$_1$). Isomer 7b: A mixture of $[OsCl_2(PPh_3)_3]$ (0.100 g, 0.0954 mmol) and **1b** (0.054 g, 0.095 mmol) in dichloromethane (10 mL) was stirred for 30 min. The volatiles were then removed under reduced pressure and the residue chromatographed on alumina, initially using a 20% mixture of THF in *n*-hexane as eluent. The THF concentration was then

increased to 50% to elute a yellow band, which was collected and the solvent removed under reduced pressure. X-ray quality crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of the product. Yield: 0.053 g (53%). IR (KBr, cm^{-1}): 3046 ν_{aromCH}; 2958, 2923, 2848 ν_{CH}; 2100 ν_{OsH}; 1580, 1431 ν_{aromCC}. NMR ($CDCl_3$, 298 K) ^1H: δ_H = –18.46 (dt, 1 H, OsH, $^2J_{PH}$ = 17, $^2J_{PH}$ = 17), 4.69 (d, 2 H, PCH_2, $^2J_{HH}$ = 13), 5.17 (d, 2 H, PCH_2, $^2J_{HH}$ = 13 Hz), 6.70-7.77 (series of multiplets, 41 H, $C_{10}H_6$ and C_6H_5). $^{13}C\{^1H\}$: δ_C = 63.6 (m, PCH_2), 106.0, 119.8 ($C_{10}H_6$), 127.2 [d, $C^{2,6}(C_6H_5)$, J_{PC} = 9], 127.8 [t^v, $C^{2,6}(C_6H_5)$, J_{PC} = 5), 128.1 [t^v, $C^{3,5}(C_6H_5)$, J_{PC} = 5], 128.3 (C_6H_5), 129.4 [d, $C^{3,5}(C_6H_5)$, J_{PC} = 15], 133.5 [t^v, $C^{3,5}(C_6H_5)$, J_{PC} = 6 Hz), 134.3-134.6, 137.0, 137.8, 140.1, 140.5 (C_6H_5 and $C_{10}H_6$, unequivocally assignable). HMBC: $\delta_C(\delta_H)$ = 211.0(–18.45) (Os=CN_2). $^{31}P\{^1H\}$: δ_P = 5.2 (m, PPh_3), 11.8 (d, PPh_2, $^2J_{PP}$ = 18 Hz). ESI-MS (+ve ion, MeCN): *m/z* = 1053.6 $[M - H]^+$, 1017.8 $[M - Cl]^+$. Accurate Mass: Found 1053.2115 $[M - H]^+$, Calcd. for $C_{55}H_{45}{}^{35}Cl^{14}N_2{}^{192}Os^{31}P_3$ 1053.2099. *Crystal data for* $C_{55}H_{46}ClN_2OsP_3$: M_r = 1053.56, triclinic, *P*–1 (no. 2), *a* = 10.347(1), *b* = 12.522(1), *c* = 20.210(2) Å, α = 82.067(5), β = 83.655(7), γ = 68.642(5)°, *V* = 2410.1(4) $Å^3$, *Z* = 2, $D_{calcd.}$ = 1.452 Mg m^{-3}, μ(Mo Kα) = 0.71 mm^{-1}, *T* = 200(2) K, yellow plate, 0.32 x 0.25 x 0.05 mm, 8334 independent reflections. F^2 refinement, R_1 = 0.065, wR_1 = 0.121 for 7147 reflections ($I > 2\sigma(I)$, $2\theta_{max}$ = 50°), 563 parameters, CCDC 996762.

Isomer 7b$_1$: Complex **7b$_1$**, proposed to be an isomer of **7b**, was generated as in the procedure described above when the reaction was carried out in THF (10 mL) instead of DCM. This resulted in a mixture of **7b** and **7b$_1$**. *NMR data for* **7b$_1$** (C_6D_6, 298 K) ^1H: δ_H = –6.23 (dt, 1 H, OsH, $^2J_{PH}$ = 85, $^2J_{PH}$ = 25), 4.21 (t^v, 4 H, PCH_2, J_{PH} = 2), 6.27 (d, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 8 Hz), 6.53-8.38 (series of multiplets, $C_{10}H_6$). $^{31}P\{^1H\}$: δ_P = –3.9 (t, PPh_3, $^2J_{PP}$ = 13), 0.1 (d, PPh_2, $^2J_{pp}$ = 13 Hz).

Synthesis of [RuHCl(CO){C(NCH$_2$PCy$_2$)$_2$C$_{10}$H$_6$}] (8). *Method 1:* A suspension of [Ru(C_6H_5)Cl(CO){$H_2C(NCH_2PCy_2)_2C_{10}H_6$}] (0.200 g, 0.240 mmol) in toluene (20 mL) was heated under reflux for 4 days. The mixture was then allowed to cool to ambient temperature, and the resulting off-white precipitate separated from the supernatant via cannula filtration. The product crystallised readily from various solvent mixtures as plates that were consistently too thin for X-ray diffractommetry. Yield: 0.115 g (64%). *Method B.* A suspension of [RuHCl(CO)(PPh_3)$_3$] (0.100 g, 1.05 mmol) and **1a** (0.064 g, 1.08 mmol) in toluene (10 mL) was heated to refluxing temperature for 20 hrs. The mixture was then allowed to cool to ambient temperature, and the solvent reduced to *ca* 5 mL. The precipitate was separated from the supernatant via cannula filtration and washed with 2-3 mL *n*-pentane. Yield: 0.046 g (58%). IR (KBr, cm^{-1}): 2924, 2851 ν_{CH}; 1992 ν_{RuH}; 1937 ν_{CO}; 1583 ν_{aromCC}. IR (DCM, cm^{-1}): 1937 ν_{CO}. NMR ($CDCl_3$, 298 K) ^1H: δ_H = –16.45 (t, 1 H, RuH, $^2J_{PH}$ = 19), 1.19-1.96 (set of multiplets, 40 H, C_6H_{11}), 2.24 (br d, 2 H, C_6H_{11}, *J* = 12), 2.54 (br, 2 H, C_6H_{11}), 4.13 (d, 2 H, PCH_2, $^2J_{HH}$ = 13), 4.41 (d, 2 H, PCH_2, $^2J_{HH}$ = 13), 6.74 (dd, 2 H, $C_{10}H_6$, $^3J_{HH}$ = 4, $^3J_{HH}$ = 4 Hz), 7.25 (d, 4 H, $C_{10}H_6$, $^3J_{HH}$ = 4 Hz). $^{13}C\{^1H\}$: δ_C = 26.2, 26.3 (C_6H_{11}), 26.8-27.1 (C_6H_{11}), 27.2 (t^v, C_6H_{11}, J_{PC} = 5), 27.8 (t^v, C_6H_{11}, J_{PC} = 6), 28.3, 29.6, 29.7 (C_6H_{11}), 35.6 (t^v, C_6H_{11}, J_{PC} = 13), 36.0 (t^v, C_6H_{11}, J_{PC} = 11), 56.9 (t^v, PCH_2, J_{PC} = 13), 106.5, 119.5, 121.2, 128.1 ($C_{10}H_6$), 134.1 [t^v, $C^{1,8}(C_{10}H_6)$, J_{PC} = 4], 134.4 ($C_{10}H_6$), 207.8 (t, RuCO, $^2J_{PC}$ = 11), 225.9 (t, Ru=CN_2, $^2J_{PC}$ = 8 Hz). $^{31}P\{^1H\}$: δ_P = 61.4. ESI-MS (+ve ion, MeCN): *m/z* = 760.3 $[M - Cl + MeCN]^+$, 719.3 $[M - Cl]^+$. Accurate Mass: Found 719.2832 $[M - Cl]^+$, Calcd. for $C_{38}H_{55}{}^{14}N_2{}^{16}O^{31}P_2{}^{102}Ru$ 719.2833. Anal. Found: C, 60.51; H, 7.38; N, 3.81%. Calcd. for $C_{38}H_{55}ClN_2OP_2Ru$: C, 60.51; H, 7.35; N, 3.71%.

Synthesis of [Ru$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_8$}Cl$_4$(η-C$_6$H$_3$Me$_3$)$_2$] (9). A solution of [$Ru_2(\mu\text{-}Cl)_2Cl_2(\eta\text{-}C_6H_3Me_3)_2$] (0.151 g, 0.258 mmol) and **1b** (0.145 g, 0.256 mmol) in dichloromethane (16 mL) was stirred for 21 hrs. After 4 h the solution had darkened, accompanied by the deposition of a brown precipitate. The solvent was removed *in vacuo* to afford a brown solid that was washed with *n*-pentane. The solid was dissolved in chloroform, filtered through a pad of diatomaceous earth and then freed of volatiles under reduced pressure to afford a brown microcrystalline solid. Yield 0.229 g (78%). Crystals suitable for crystallographic analysis were obtained from vapour diffusion of *n*-hexane into a solution of the complex in $CHCl_3$. IR (ATR, cm^{-1}): 3050 ν_{aromCH}, 1585 ν_{aromCC} cm^{-1}. NMR ($CDCl_3$, 298 K) ^1H: δ_H = 1.93 (s, 18 H, CH_3), 3.42 (s, 2 H, N_2CH_2), 4.38 (br s, 4 H, PCH_2), 4.60 (s, 6 H, C_6H_3), 5.76 (d, 2 H, $^3J_{HH}$ = 7.2, $C_{10}H_6$), 6.61 (m, 4 H, $C_{10}H_6$), 7.39 (m, 12 H, C_6H_5), 7.88 (m, 8 H, C_6H_5). $^{13}C\{^1H\}$: δ_C = 18.6 (CH_3), 49.8 (d, $^1J_{PC}$ = 24, PCH_2), 66.6 (N_2CH_2), 85.5 (d, $^2J_{PC}$ = 3, C_6H_3), 102.4 ($C_{10}H_6$), 102.7 (d, $^2J_{PC}$ = 2, C_6H_3), 112.7, 115.5, 125.9 ($C_{10}H_6$), 128.2 [d, $^2J_{PC}$ = 9, $C^{2,6}(C_6H_5)$], 130.2 [d, $^1J_{PC}$ = 40, $C^1(C_6H_5)$], 131.3 [d, $^4J_{PC}$ = 2, $C^4(C_6H_5)$], 134.2 [d, $^3J_{PC}$ = 9, $C^{3,5}(C_6H_5)$], 140.5 [d, $^3J_{PC}$ = 3 Hz, $C^{1,8}(C_{10}H_6)$]. $^{31}P\{^1H\}$: δ_P = 23.6. ESI-MS (+ve ion, MeCN): *m/z*: 1151.1 $[M + H]^+$. Accurate Mass: Found 1151.0842 $[M + H]^+$, Calcd. for $C_{55}H_{57}N_2P_2{}^{35}Cl_4{}^{102}Ru_2$ 1151.0838. Anal. found: C, 57.48; H, 5.01; N, 2.25%. Calcd. for $C_{55}H_{56}N_2P_2Ru_2Cl_4$: C, 57.40; H, 4.90; N, 2.43%. *Crystal data for* $C_{55}H_{56}Cl_4N_2P_2Ru_2.CHCl_3$: M_w = 1270.34, triclinic, *P*-1 (no.2), *a* = 14.8173(4), *b* = 14.9752(4), *c* = 24.0480(6) Å, α = 89.776(2), β = 89.386 (2), γ = 87.798(1)º, *V* = 5331.8(2) $Å^3$, *Z* = 4, $D_{calcd.}$ = 1.582 Mg m^{-3}, μ(Mo Kα) = 1.02 mm^{-1}, *T* = 200 (2) K, red block, 0.20 x 0.14 x 0.11 mm, 18877 independent reflections. F^2 refinement, R_1 = 0.116, wR_2 = 0.273 for 13227 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 50º), 1241 parameters (CCDC 1039761).

Synthesis of [Au$_2${μ-H$_2$C(NCH$_2$PPh$_2$)$_2$C$_{10}$H$_8$}Cl$_2$] (10). A solution of [AuCl(THT)] (0.201 g, 0.627 mmol) and **1b** (0.177 g, 0.312 mmol) in dichloromethane (25 mL) was stirred at room temperature for 20 hrs. The solvent was removed *in vacuo* to afford a brown solid that was washed with *n*-hexane and dried under vacuum overnight. The crude product was dissolved in chloroform, layered with *n*-pentane and covered in aluminium foil overnight. Precipitation of colloidal gold coated the bottom of the flask, and the remaining solution was decanted into a conical flask. Slow evaporation produced white-pale yellow crystals that were washed with *n*-pentane and dried under high vacuum. Yield 0.080g (25%). Crystals suitable for crystallographic analysis were obtained from vapor diffusion of *n*-pentane into a solution of **10** in $CHCl_3$. IR (ATR, cm^{-1}) 3046 ν_{aromCH}, 1590 ν_{aromCC}. NMR ($CDCl_3$, 298 K) ^1H: δ_H = 4.40 (s, 4

H, PCH_2), 4.53 (s, 2 H, N_2CH_2), 6.38 [d, 2 H, $^3J_{HH}$ = 7.6 Hz, $H^{2,7}(C_{10}H_6)$], 7.19 (m, 2 H, $C_{10}H_6$), 7.28 (m, 2 H, $C_{10}H_6$), 7.45 (m, 12 H, C_6H_5), 7.76 (m, 8 H, C_6H_5). $^{13}C\{^1H\}$: δ_C = 52.4 (d, $^1J_{PC}$ = 43, PCH_2), 68.0 (N_2CH_2), 108.6, 117.5, 120.6, 126.4 ($C_{10}H_6$), 128.0 [d, $^1J_{PC}$ = 57, $C^1(C_6H_5)$], 129.4 [d, $^2J_{PC}$ = 11, $C^{2,6}(C_6H_5)$], 132.3 [d, $^4J_{PC}$ = 3, $C^4(C_6H_5)$], 133.9 [d, $^3J_{PC}$ = 13, $C^{3,5}(C_6H_5)$], 135.0 ($C_{10}H_6$), 141.5 [d, $^3J_{PC}$ = 2 Hz, $C^{1,8}(C_{10}H_6)$]. $^{31}P\{^1H\}$: δ_P = 20.0. ESI-MS (+ve ion, MeCN): *m/z*: 1031.1 [M + H]$^+$. Accurate Mass: Found 1057.0586 [M + Na]$^+$, Calcd. for $C_{37}H_{32}N_2{}^{23}NaP_2{}^{37}Cl_2{}^{197}Au_2$ 1057.0588. Anal. found: C, 43.22; H, 3.10; N, 2.79%. Calcd. for $C_{37}H_{32}N_2P_2Cl_2Au_2$: C, 43.09; H, 3.13; N, 2.72%. *Crystal data* for $C_{37}H_{32}Au_2Cl_2N_2P_2.2(CHCl_3)$: M_w = 1270.21, monoclinic, $P2_1/a$, a = 11.1480(1), b = 23.5178(4), c = 16.5354(3) Å, β = 100.1676(8)°, V = 4267.1(1) Å^3, Z = 4, $D_{calcd.}$ = 1.977 Mg m^{-3}, μ(Mo $K\alpha$) = 7.48 mm^{-1}, T = 200(2) K, colourless lath, 0.35 x 0.17 x 0.05 mm, 9800 independent reflections. F^2 refinement, R_1 = 0.067, wR_2 = 0.180 for 8386 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 55°), 478 parameters, CCDC 1039835.

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Notes and references

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14 Although these results are outside the range viewed as establishing analytical purity (±0.4%), they are provided to illustrate the best values obtained to date.

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Double geminal aminal C–H activation processes of the dihydroperimidine based NHC pincer pro-ligands $H_2C(NCH_2PR_2)_2C_{10}H_6$ are described leading to dihydroperimidinylidene complexes including the first osmium examples.

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