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ARTICLE

Synthesis and Ligand Substitution Reactions of κ⁴-*B,S,S′,S″*-Ruthenaboratranes

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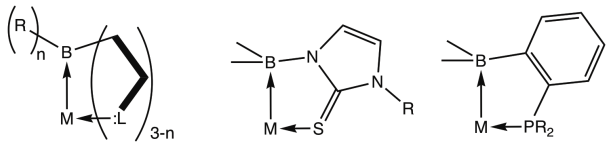
A range of ruthenaboratranes of the form [Ru(CO)L{κ⁴-*B,S,S′,S″*-B(mt)₃}] (mt = *N*-methylmercaptoimidazolyl) have been prepared either by substitution of the PPh_3 ligand in [Ru(CO)(PPh_3){κ⁴-*B,S,S′,S″*-B(mt)₃}] by L (L = PMe_2Ph, PMe_3, $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$) or reactions of [RuCl(R)(CO)L_n] (R = Ph, CH=CHPh; n = 2 L = PCy_3; n = 3 L = $P(OMe)_3$, PMe_2Ph) with Na[HB(mt)₃].

Introduction

Metallaboratranes[1] are cage structures in which a transannular dative (polar covalent,[2] M→B) bond between a transition metal and boron is supported by two or three buttressing bridges (Chart 1). Metallaboratranes with *N*-heterocyclic buttresses are known for all the elements of groups 8,[3,4q] 9,[4] 10[5] and 11,[6] with the majority of studies involving the heavier elements of group 9.[4] In contrast, despite the archetype [Ru(CO)(PPh_3){κ⁴-*B,S,S′,S″*-B(mt)₃] (**1a** mt = *N*-methyl-2-mercaptoimidazolyl),[3b,7] being based on ruthenium, very few further examples have been described within group 8, these being limited to Parkin's ferraboratrane [Fe(CO)₂{B(mt^{tBu})₃}],[3a] the osmaboratrane analogue of **1a**,[3f] the ruthenaboratranes [Ru(CS)(PPh_3){κ⁴-*B,S,S′,S″*-B(mt)₃] (**2**) and [Ru(CO)(CNR){B(mt)₃] (R = ^{t}Bu **1c**, $C_6H_3Me_2$-2,6 **1d**, $C_6H_2Me_3$-2,4,6 **1e**),[4c] and the *N*-chlorophenyl analogue of **1a**.[4d]



Metallaboratrane (n = 0,1; R= H, Ph) | *N*-R-mercaptoimidazolyl-metallaboratranes | 2-Phosphinoaryl-metallaboratranes

Chart 1. The metallaboratrane motif.

The poly(2-phosphinophenyl)borane scaffold pioneered by Bourissou[8] has been applied to metals from groups 9,[8,9] 10[10] and 11[11] but it is with iron, as developed by Peters,[12] that the ligand system has enjoyed the most intense study, rewarded with impressive results in supporting *inter alia* the stoichiometric reduction of CO and the catalytic reduction of N_2.

This dearth of group 8 metallaboratranes is perhaps counter-intuitive in that of all the late transition metals, those of group 8 in the formally zerovalent state[13] are likely to be the strongest σ-bases and best able to stabilise the Lewis acidic boron through *Z*-type polar-covalent bonding.[14] We therefore contend that the scarcity of group 8 *(M→B)*[8] metallaboratranes[15] is an historical oversight rather than any reflection on their stability or accessibility. Accordingly, we describe herein the synthesis of a range of new ruthenaboratranes for the purpose of assessing the varying impact of co-ligands upon the *(Ru→B)*[8] dative interaction.

Results and Discussion

The first metallaboratrane, **1a**, arose from the unexpected reaction of [RuCl(R)(CO)(PPh_3)₂] (R = Ph, CH=CHPh) with Na[HB(mt)₃] *via* activation of the borohydride group and elimination of benzene or styrene.[3b,c] The B–H activation step is presumed to proceed *via* coordination of this group to the ruthenium centre *via* a 3 centre 2-electron B–H···Ru association, isolable related examples of which include the complexes [RuH(CO)(PPh_3){κ³-*H,S,S′*-HB(mt)₃}][3d] [RuH(PPh_3)₂{κ³-*H,S,S′*-H_2B(mt)₂}][16a] and [RuX(CO)(PPh_3){κ³-*H,S,S′*-H_2B(mt)₂}] (X = H, Cl, SePh, $SiCl_3$, $SiMe_3$, $BO_2C_6H_4$).[16b] The factors that dictate why in some but by no means all cases this coordination mode proceeds to B–H activation and metallaboratane formation are not well delineated, though the reverse process, *i.e.*, migration of a hydride ligand to a *cis* M→B bond has been observed on rare occasions for platina-,[5c,i] rhoda-[4r,9e] and ferraboratranes.[12] It may well be therefore that this process does indeed surreptitiously operate more widely and reversibly but not to spectroscopically determinable extents.

Perhaps surprisingly, the phosphine ligand in **1a** was shown to be labile under mild conditions, being reversibly displaced by CO to provide [Ru(CO)₂{κ⁴-*B,S,S′,S″*-B(mt)₃] (**1b**) which however reverted to **1a** under vacuum. Irreversible substitution however ensued with isonitriles to provide a [Ru(CO)(L){κ⁴-*B,S,S′,S″*-B(mt)₃}] (L = CN^{t}Bu **1c**, $CNC_6H_3Me_2$-2,6 **1d**, $CNC_6H_2Me_3$-2,4,6 **1e**).[3c] The syntheses of new ruthenaboratranes to be described

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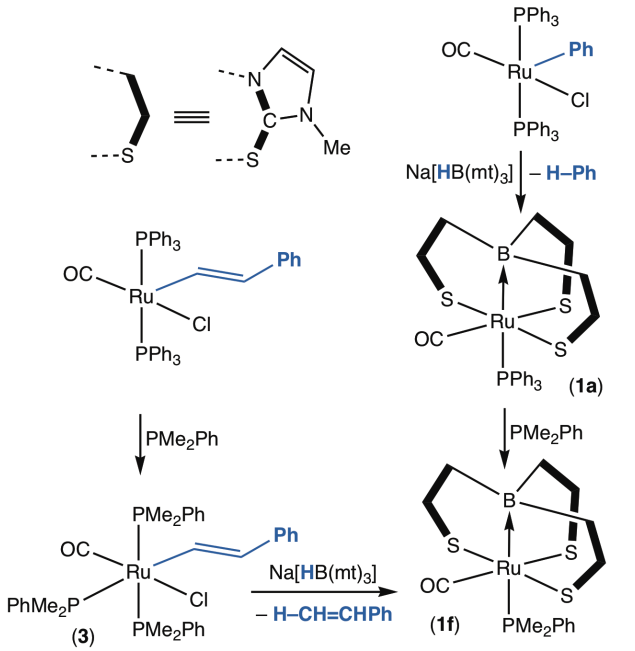
†Electronic Supplementary Information (ESI) available: Crystallographic information files CCDC 1874175 – 1874179 relate to compounds discussed herein.

herein therefore take one of two different approaches; either (i) ligand substitution reactions of **1a** with a range of phosphines or (ii) pre-installation of the phosphine prior to ruthenaboratrane assembly.

Treating a solution of **1a** with a slight excess of PMe_2Ph in dichloromethane at room temperature results in complete phosphine substitution with the formation of $[Ru(CO)(PMe_2Ph)\{\kappa^4\text{-}B,S,S',S''\text{-}B(mt)_3\}]$ (**1f**, Scheme 1).



Scheme 1. Alternative syntheses of $[Ru(CO)(PMe_2Ph)\{B(mt)_3\}]$ (**1f**).

Alternatively, **1f** may be prepared by installing PMe_2Ph prior to the ruthenaboratrane assembly. Mawby has described the synthesis of *mer*-$[RuCl(Ph)(CO)(PMe_2Ph)_3]$ *via* the reaction of $[RuCl(Ph)(CO)(PPh_3)_2]$ with excess PMe_2Ph[17] and a similar protocol converts $[RuCl(CH{=}CHPh)(CO)(PPh_3)_2]$[18] to *mer*-$[RuCl(CH{=}CHPh)(CO)(PMe_2Ph)_3]$ **3** in 79% yield (Scheme 1). The characterisation of **3** included a crystallographic analysis (Figure 1) and is generally unremarkable other than to note that (i) the *mer*-RuP_3 geometry is confirmed both crystallographically and from $^{31}P\{^1H\}$ NMR data ($CDCl_3$: δ_P = –8.80 t, –1.17 dt, $^2J_{PP}$ = 23.1 Hz) and (ii) The σ-styryl ligand, as expected for a σ-organyl, exerts a discernible *trans* influence upon the unique phosphine (Ru1–P2 = 2.4148(9) Å) relative to the mutually *trans* disposed pair of phosphines, however the significant disparity between these two Ru–P bonds (Ru1–P1 = 2.3573(9), Ru1–P3 = 2.3971(9) Å) is itself noteworthy given their spectroscopic chemical equivalence. A search for inter- or intramolecular close-contacts failed to identify any interactions that might be responsible, leading us to conclude that this is simply a response to

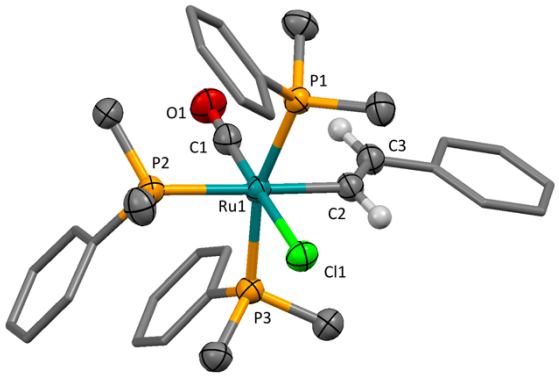


Figure 1. Molecular structure of **3** (Most hydrogen atoms omitted, phenyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ru1–Cl1 2.4815(8), Ru1–P1 2.3573(9), Ru1–P2 2.4148(9), Ru1–P3 2.3971(9), Ru1–C1 1.818(4), Ru1–C2 2.106(3), C2–C3 1.329(5), C3–C4 1.483(5), Cl1–Ru1–P1 86.33(3), Cl1–Ru1–P2 93.18(3), P1–Ru1–P2 97.53(3), Cl1–Ru1–P3 83.66(3), P1–Ru1–P3 163.10(3), P2–Ru1–P3 96.59(3), P1–Ru1–C1 92.59(12), P2–Ru1–C1 87.82(11), P3–Ru1–C1 97.18(12), Cl1–Ru1–C2 88.6(1), P1–Ru1–C2 82.4(1), P3–Ru1–C2 83.73(9), C1–Ru1–C2 90.44(15), Ru1–C2–C3 130.1(3), C2–C3–C4 126.9(3).

meridionally accommodating the three irregularly shaped phosphines.

Heating **3** with $Na[HB(mt)_3]$ in THF under reflux for 12 hours returns **1f** in 51% yield. The phosphine associated resonance which appear at δ_P = –13.3 ($CDCl_3$) in the $^{31}P\{^1H\}$ NMR spectrum of **1f** is conspicuously broad consistent with coordination *trans* to the quadrupolar boron of the metallaboratrane. The $^{11}B\{^1H\}$ NMR spectrum comprises an apparent singlet resonance ($CDCl_3$: δ_B = 15.4), the broadness of which precluded the resolution of $^2J_{PB}$. The molecular geometry of **1f** is depicted in Figure 2 and geometric features will be discussed collectively alongside other examples to follow.

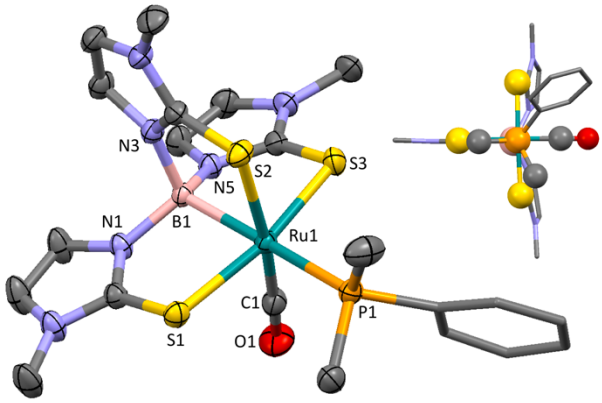
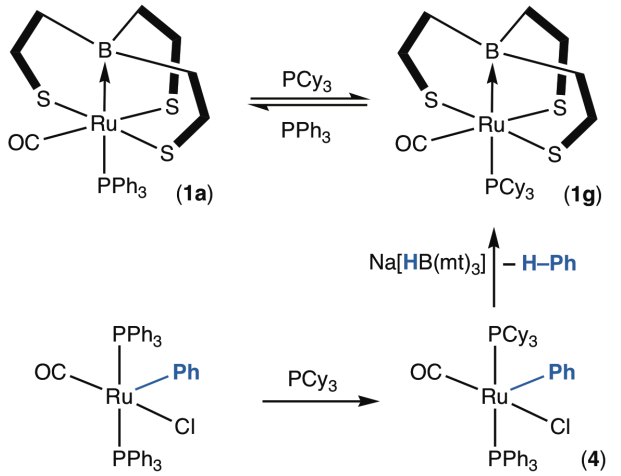


Figure 2. Molecular structure of **1f** (Hydrogen atoms omitted, phenyl and methimazolyl groups simplified, 50% displacement ellipsoids). Inset = view along Ru1···P1 vector. Selected bond lengths (Å) and angles (°): B1–Ru1 2.174(3), B1–N1 1.561(4), B1–N3 1.580(4), B1–N5 1.561(4), Ru1–S1 2.3881(7), Ru1–S2 2.4938(7), Ru1–S3 2.4071(8), Ru1–P1 2.4170(7), Ru1–B1–N1 110.41(18), Ru1–B1–N3 110.57(18), N1–B1–N3 105.7(2), Ru1–B1–N5 109.74(18), N1–B1–N5 114.5(2), N3–B1–N5 105.7(2) B1–Ru1–S1 83.44(8), B1–Ru1–S2 85.21(8), S1–Ru1–S2 90.92(3), B1–Ru1–S3 82.84(8).

Whilst the replacement of PPh_3 in **1a** by the more compact and strongly σ-basic phosphine PMe_2Ph proceeded quickly under mild conditions, the same reaction involving the more sterically demanding phosphine PCy_3 did not proceed to

completion but rather afforded an equilibrium mixture of **1a** and [Ru(CO)(PCy_3){κ⁴-*B,S,S',S''*-B(mt)$_3$}] (**1g**, Scheme 2).



Scheme 2. Alternative syntheses of [Ru(CO)(PCy_3){B(mt)$_3$}] (**1g**).

This mixture proved too problematic to separate and accordingly the alternative pre-installation approach was found to be preferable. Aerobic decomposition of Grubbs' catalyst [$RuCl_2$(=CHPh)(PCy_3)$_2$] has been shown to provide [RuCl(Ph)(CO)(PCy_3)$_2$] (**4**),[19] but in the present work **4** was more conveniently obtained in 80% yield simply by heating [RuCl(Ph)(CO)(PPh_3)$_2$] with excess PCy_3. The reaction of **4** with Na[HB(mt)$_3$] in dichloromethane proceeds to completion within 2 hours to cleanly provide **1g** in 77% yield, obviating the PPh_3 and **1a** contamination problems encountered in the initial route. The molecular structure of **1g** is shown in Figure 3, from which the steric bulk of the PCy_3 ligand is immediately obvious relative to that of the phosphines in **1a** and **1f** (*vide infra*, Figure 7).

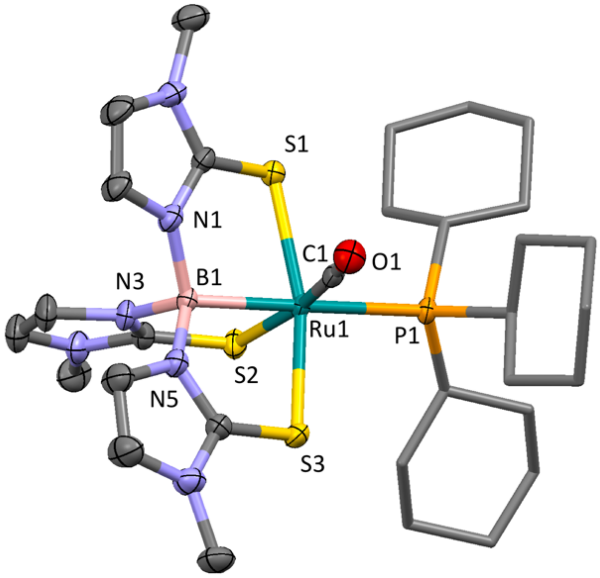


Figure 3. Molecular structure of **1g** in a crystal of **1g**.CH_2Cl_2 (Hydrogen atoms and solvent omitted, cyclohexyl and methimazolyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): B1–Ru1 2.168(3), B1–N1 1.568(4), B1–N3 1.568(4), B1–N5 1.560(5), Ru1–S1 2.4188(8), Ru1–S2 2.4922(8), Ru1–S3 2.4084(8), Ru1–P1 2.4894(7), Ru1–B1–N1 110.4(2), Ru1–B1–N3 110.2(2), N1–B1–N3 105.6(2), Ru1–B1–N5 111.2(2), N1–B1–N5 112.6(3), N3–B1–N5 106.6(3), B1–Ru1–S1 81.45(10), B1–Ru1–S2 85.49(10), S1–Ru1–S2 89.83(3), B1–Ru1–S3 83.36(10), S1–Ru1–S3 164.73(3), S2–Ru1–S3 90.59(3).

In contrast to the steric encumbrance and high σ-basicity of the PCy_3 ligand in **1g**, the more compact derivative [Ru(CO)(PMe_3){B(mt)$_3$}] (**1h**) was obtained *via* simple substitution of PPh_3 in **1a** by PMe_3. The molecular geometry of **1h** is shown in Figure 4 and data are discussed collectively below. Notably, in contrast to the reversible reaction of **1a** with CO to provide **1b** and its irreversible reaction with CN^{t}Bu, to afford **1c**, the PMe_3 ligand in **1h** is displaced by neither CO nor CN^{t}Bu under ambient conditions (CH_2Cl_2, 12hrs).

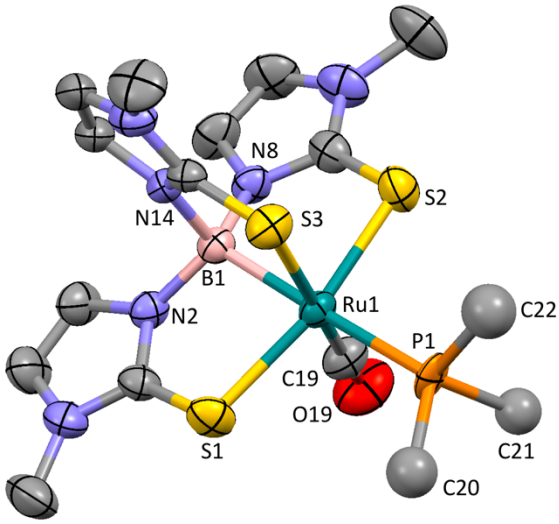


Figure 4. Molecular structure of **1h** in a crystal (Hydrogen atoms and solvent omitted, , 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ru1–B1 2.157(6), Ru1–S2 2.3929(17), Ru1–S1 2.4068(17), Ru1–P1 2.423(7), Ru1–S3 2.5103(15), B1–N2 1.558(7), B1–N8 1.559(8), B1–N14 1.587(8), B1–Ru1–S2 83.35(17), B1–Ru1–S1 82.90(17), B1–Ru1–S3 85.45(17), N2–B1–N8 114.0(4), N2–B1–N14 104.6(4), N8–B1–N14 105.3(4). The PMe_3 ligand was disordered over three positions (ca 46, 32 and 22% occupancy) with the major occupancy isotropically refined components shown.

Of the three phosphines in **1a**, **1f**, **1g** and **1h**, PCy_3 has the lowest Tolman electronic parameter[20] which is also reflected in **1g** having the lowest ν_{CO} value (CH_2Cl_2: 1876 cm^{-1}), well within the region typical of zerovalent ruthenium complexes. Having prepared two ruthenaboratranes with strongly σ-basic phosphines with small (PMe_3, θ_T = 118°) and large (PCy_3: θ_T = 170°) Tolman cone angles[20] we next turned to phosphorus ligands with modest steric profiles but reduced donor strength, *i.e.*, phosphites (Chart 2) to broaden the ligand space under consideration.

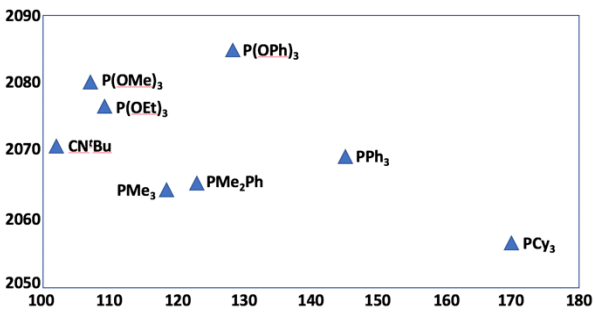
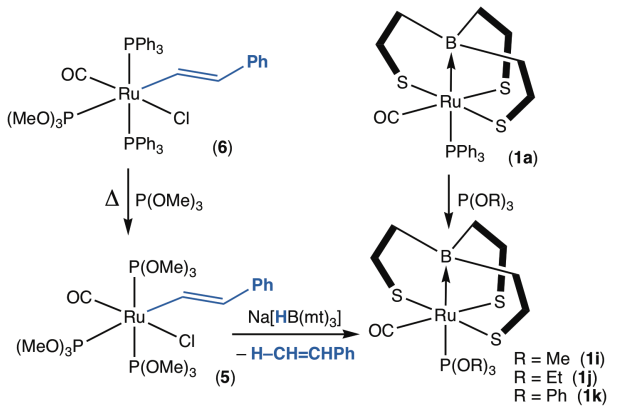


Chart 2. Distribution of Phosphines Employed Across Tolman Steric (θ_T) and Electronic (ν_T) Space

Both synthetic approaches described above proved successful, though in both cases more forcing conditions and extended reaction times were required to complete the conversions. Thus **1a** reacted with $P(OMe)_3$ to provide modest yields of $[Ru(CO)\{P(OMe)_3\}\{B(mt)_3\}]$ (**1i**, Scheme 3) when heated for 16 hours in refluxing hexane (59%) or THF (49%).



Scheme 3. Alternative syntheses of $[Ru(CO)\{P(OR)_3\}\{B(mt)_3\}]$ (R = Me **1i**, Et **1j**, Ph **1k**).

Similar results were obtained for the formation of triethyl (**1j**) and triphenyl (**1k**) analogues. Complex **1i** failed to provide crystallographic grade crystals however both **1j** (Figure 5) and **1k** (Figure 6) were structurally characterised and their structural features are discussed below. Passing a stream of CO through a dichloromethane solution of **1i** results in *ca* 30 % conversion to $[Ru(CO)_2\{B(mt)_3\}]$ (**1b**: 2020, 1994 cm^{-1}) which was however cleanly converted back to **1i** when the CO stream was replaced with a nitrogen purge, or the sample simply left to evaporate.

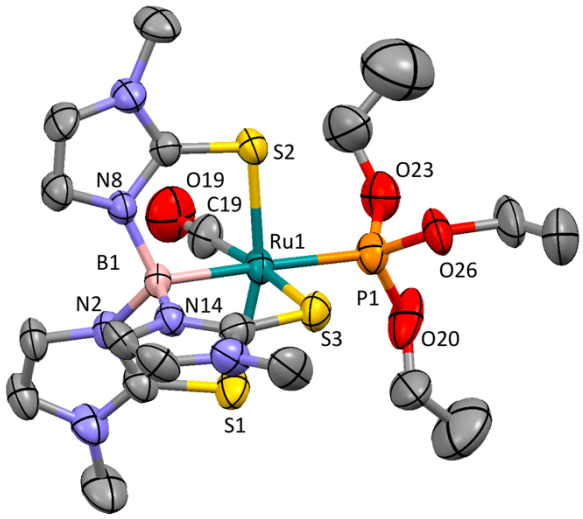


Figure 5. Molecular structure of **1j** (Hydrogen atoms omitted, groups simplified, 50% displacement ellipsoid). Selected bond lengths (Å) and angles (°): Ru1–B1 2.172(6), Ru1 P1 2.360(6), Ru1–S2 2.4018(16), Ru1–S1 2.4306(19), Ru1–S3 2.4781(17), B1–N8 1.559(8), B1–N2 1.560(8), B1–N14 1.571(8), B1–Ru1–S2 83.45(18), B1–Ru1–S1 80.79(19), B1–Ru1–S3 85.33(18), N8–B1–N2 112.6(5), N8–B1–N14 104.9(5), N2–B1–N14 107.8(5). Each OEt group suffers position disorder, with only the major occupancy components shown

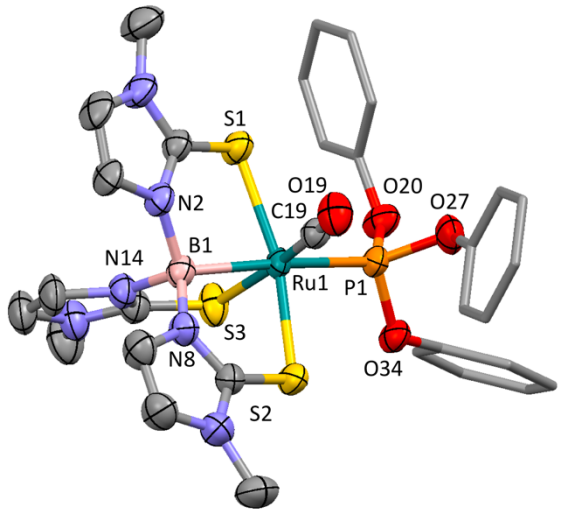


Figure 6. Molecular structure of **1k** (Hydrogen atoms omitted, phenyl groups simplified, 50% displacement ellipsoids). Selected bond lengths (Å) and angles (°): Ru1–B1 2.184(6), Ru1–P1 2.314(4), Ru1–S2 2.4048(14), Ru1–S1 2.4167(13), Ru1–S3 2.4776(14), B1–N14 1.564(7), B1–N8 1.568(7), B1–N2 1.568(7), B1–Ru1–S2 82.88(15), B1–Ru1–S1 81.54(15), B1–Ru1–S3 85.02(15), N14–B1–N8 107.3(4), N14–B1–N2 104.8(4), N8–B1–N2 113.5(4). Each OPh group suffers position disorder, with only the major occupancy components shown.

Alternatively, *mer*-$[RuCl(CH{=}CHPh)(CO)\{P(OMe)_3\}_3]$ (**5**) was prepared by heating $[RuCl(CH{=}CHPh)(CO)(PPh_3)_2]$[18] with excess $P(OMe)_3$ in hexane under reflux for 16 hours as described previously for the synthesis of $[RuCl(Ph)(CO)\{P(OMe)_3\}_3]$.[17] Although the yield of this conversion was spectroscopically quantitative, the high solubility compromised the isolated yield (59%). Reduced reaction times provide samples contaminated with *mer-trans*-$[RuCl(CH{=}CHPh)(CO)(PPh_3)_2\{P(OMe)_3\}]$ (**6**) which could be acquired in pure form *via* reaction of $[RuCl(CH{=}CHPh)(CO)(PPh_3)_2]$ with one equivalent of $P(OMe)_3$ at room temperature. The *mer*-RuP_3 geometry of **5** was confirmed by $^{31}P\{^1H\}$ NMR spectroscopy (**AB_2**: δ_P = 128.9 d, 142.4 t, $^2J_{AB}$ = 43.0 Hz). Heating **6** with $Na[HB(mt)_3]$ in refluxing THF for 12 hours afforded **1i** in 59% yield. As with the other derivatives, the resonance for the phosphite in the $^{31}P\{^1H\}$ NMR spectrum was broadened (δ_P = 159.1) indicating coupling between the ^{31}P and quadrupolar ^{11}B nuclei, however the ^{11}B resonance (δ_B = 15.4) was not much moved from those for derivatives with more σ-basic (less π-acidic) phosphines. These and other spectroscopic data are collated in Table 1.

Table 1. Tolman Steric (θ_T) and Electronic (ν_T) parameters for phosphines and selected structural data for ruthenaboratranes $[Ru(CO)(L)\{B(mt)_3\}]$ (**1**)

L	θ_T	ν_T	ν_{CO}	δ_B	r_{RuB}	r_{RuP}
PCy_3	170	2056.4	1876	15.4	2.168(3)	2.4894(7)
PPh_3	145	2068.9	1894	17.1	2.161(5)	2.435(1)
$P(OPh)_3$	128	2085.3	1923	13.0	2.184(6)	2.314(4)
PMe_2Ph	122	2065.3	1887	15.4	2.174(3)	2.4170(7)
PMe_3	118	2064.1	1885	14.6	2.157(6)	2.423(7)
$P(OEt)_3$	108	2076.3	1904	14.0	2.172(6)	2.360(6)
$P(OMe)_3$	107	2079.5	1907	14.5	–	–
CN^tBu	102[a]	2071.3[b]	1894	14.6	2.176(7)	–

[a]Taken from reference 21. [b]$[Ni(CN^tBu)(CO)_3]$ has not been reported, the value given here is for $[Ni(CN^nBu)(CO)_3]$.[22].

The comparative π-acidity of the phosphite relative to phosphines is, however, indirectly manifested in the ν_{CO} values (CH_2Cl_2: **1i** 1907, **1k** 1923 cm^{-1}) being the highest for the series,. Taking the range of ruthenaboratranes together, Table 1 collates the two key structural features, *i.e.*, the bond lengths between ruthenium and phosphorus or boron, contextualised by the Tolman steric and electronic parameters.[20]

Despite Tolman's electronic parameter being derived from the A_1 vibrational mode for C_{3v}-[$Ni(CO)_3(PR_3)$] complexes,[20] there is good correlation between this and the single ν_{CO} value for the complexes **1** (Chart 3).

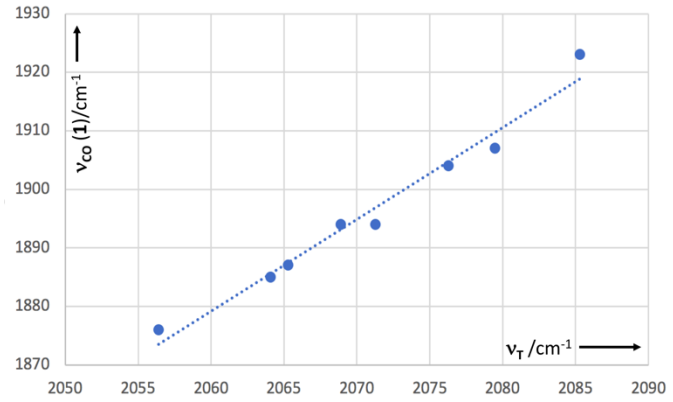


Chart 3. Correlation of ν_{CO} for ruthenaboratranes (**1**) *vs* Tolman's Electronic Parameter ν_T. [$Ni(CN^tBu)(CO)_3$] has not been reported, the value used here is for [$Ni(CN^nBu)(CO)_3$].[22]

Chart 4 presents Ru–B bond lengths in relation to the ν_{CO} values for ruthenaboratranes. The isonitrile and phosphite ligands have the capacity to act as π-acceptors and the three derived complexes display the longest Ru–B bond lengths, however the PMe_2Ph derivative **1f** has a Ru–B bond length comparable to that of the CN^tBu and $P(OEt)_3$ derivatives, but considerably longer than found in the PMe_3 derivative (**1i**) despite PMe_3 and PMe_2Ph having rather similar ν_T values.

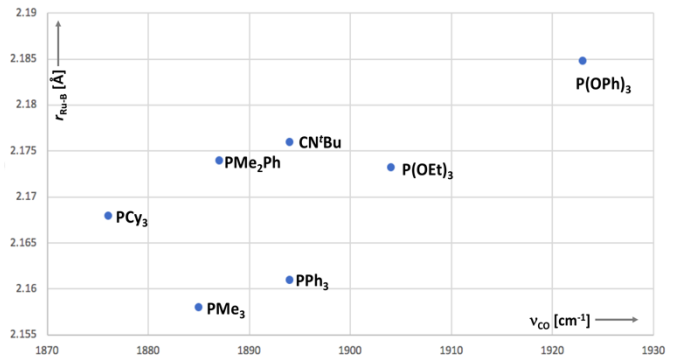


Chart 4. Relationship between Ru–B bond length and ν_{CO} for ruthenaboratranes (**1**)

Although PCy_3 is considered more electron releasing than PMe_3, the Ru–B bond length in the PCy_3 derivative **1g** is intermediate between those for the PMe_3 (**1h**) and PMe_2Ph (**1f**) derivatives (Chart 4), presumably due to the more pronounced inter ligand repulsion in the PCy_3 complex. Steric factors should be more pronounced in octahedral ruthenium complexes than in tetrahedral [$Ni(CO)_3(PR_3)$] and the selection of phosphines spans a wide range ($107 < \theta_T < 170°$). Figure 7 presents space filling representations for the phosphines considered in addition to the two previously reported isonitrile derivatives [Ru(CO)(CNR){$B(mt)_3$}] (R = ^{t}Bu, $C_6H_2Me_3$-2,4,6).[3c] Whilst isonitriles are clearly more slender ligands than the vast majority of phosphines, they also present a variable degree of π-acidity depending on the nature of the alkyl or aryl substituent.

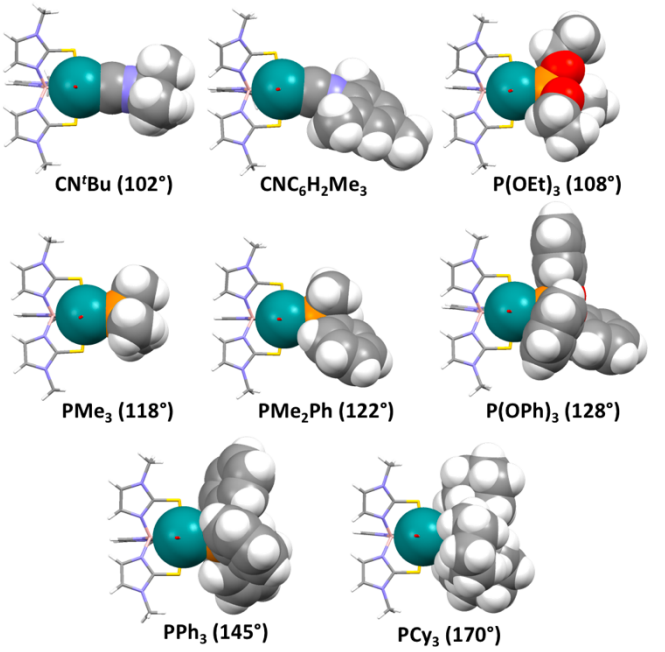


Figure 7. Space-filling representations of ligands bound to the 'Ru(CO){$B(mt)_3$}' viewed along the unique Ru–C vector with associated Tolman cone angles (θ_T).

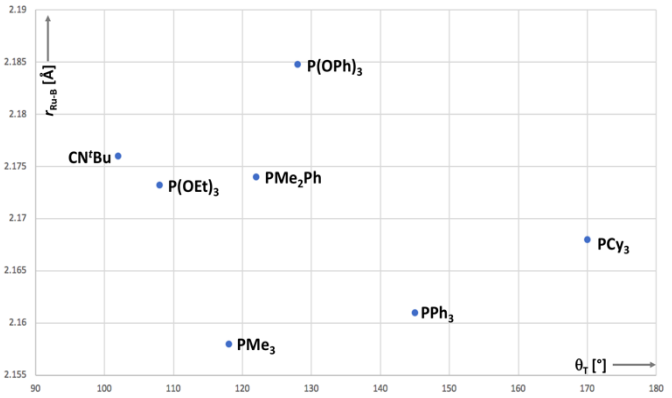


Chart 5. Relationship of ruthenaboratrane Ru–B bond length towards θ_T for phosphines (**1**)

Finally, it may be noted that there is no useful correlation between the Ru–S bond lengths and either the Tolman cone angle or the Ru–B bond length (See Supporting Information, Chart S1), as might be expected given the comparatively narrow ranges spanned (*trans*-S-Ru–S: 2.478 – 2.510 = 0.032 Å; *trans*-L-Ru–S: 2.398 – 2.417 = 0.02 Å; Ru–B: 2.157 – 2.184 = 0.027 Å) and the typical precision in these bond lengths (6 x e.s.d. = *ca* 0.004 – 0.011 (Ru–S) and 0.018 – 0.036 Å). In all cases, however, the

unique Ru–S bond length is significantly longer (*ca* 0.08 Å) than the average of the two mutually trans disposed Ru–S bonds.

Conclusions

Despite significantly extending the range of known ruthenaboratranes and acquiring both spectroscopic and crystallographic data for many, not a single parameter emerges as a definitive measure of the variable degree of Ru→B interaction. The Tolman steric and electronic parameters are independent variables that may reinforce or counteract each other with respect to the Ru–B bond length (and by implication, bond strength). Whilst the bridgehead boron nuclei give rise to resonances in a region of the ^{11}B NMR spectra appropriate for four-coordinate boron, these span a remarkably small range and are exacerbated by the typically broad appearance of resonances. Each example includes a carbonyl ligand coordinated *cis* to both the variable phosphine and the borane boron, however other than correlating, as expected with the Tolman electronic parameter,[20] the values for ν_{CO}, which span almost 50 cm^{-1} for the series, show no significant correlation with geometric parameters such as r_{RuB}. There is a rather loose inverse correlation between r_{RuB} and r_{RuP}, however this may well be a response to steric rather than electronic factors. That said, the shortest Ru–B separation observed amongst the phosphine/phosphite series corresponds to the smallest *and* most σ-basic PMe_3 derivative. The shortest case overall however involves the isonitrile $CNC_6H_2Me_3$-2,4,6 which has a Tolman 'cone angle' estimated to be comparable (116°) to PMe_3 (118°) although somewhat less electron releasing due to a degree of synergic σ-donor/π-acceptor bonding.

We are therefore at this stage forced to resort to the chemists' standard conclusion; *a subtle interplay of steric and electronic factors.*

Experimental

General Considerations. Unless otherwise stated, all experimental work was carried out at room temperature under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line and inert atmosphere (argon) dry-box techniques. Solvents tetrahydrofuran, toluene, pentane and hexane were dried and distilled under a nitrogen atmosphere from benzophenone and sodium. Dichloromethane was dried and distilled under a nitrogen atmosphere from calcium hydride. The silica gel used for chromatography was dried in an oven at 100°C, evacuated and saturated with nitrogen prior to use. Once isolated, compounds were generally stored as solids under a nitrogen or argon atmosphere at –20°C. NMR spectra were obtained at 25°C on Jeol JNM EX 270 (^{1}H at 270.0, ^{13}C at 67.9 MHz, ^{11}B at 86.6, ^{31}P at 109.3 MHz), Bruker AVANCE 400 (^{1}H at 399.9 MHz), Bruker AVANCE 600 (^{1}H at 600.0, ^{13}C NMR at 150.9 MHz) or Bruker AVANCE 800 (^{1}H at 800.1, ^{13}C NMR at 201.0 MHz) spectrometers. Chemical shifts (δ) are reported in ppm and referenced to the solvent peaks or external standards (^{31}P: 70 % H_3PO_4; ^{11}B: $BF_3.OEt_2$). The multiplicities of NMR resonances are denoted by the abbreviations s (singlet), d (doublet), t (triplet), m (multiplet) and combinations thereof for more highly coupled systems. Infrared spectra were obtained using a Perkin-Elmer 1720-X or Spectrum One FT-IR spectrometers. FAB mass spectra were obtained from 3-nitrobenzylalocohol matrices with Kratos MS-80 or Autospec-Q instrument. Electrospray ionisation mass spectrometry (ESI-MS) was performed by the ANU Research School of Chemistry mass spectrometry service with acetonitrile as the matrix. With the exception of complexes **1h**, **1j** and **1k**, data for X-ray crystallography were collected on Nonius Kappa KappaCCD, Oxford Diffraction Xcalibur or SuperNova diffractometers. Diffraction data for complexes **1h**, **1j** and **1k** were collected some years ago at room temperature on a Siemens P4 diffractometer using sealed tube X-ray sources and single point counter detectors. As such, the data beyond 2θ *ca* 120° with copper radiation, or *ca* 45° with molybdenum radiation was typically too weak and diffuse to be observable in a sensible time frame, and so the standard data collections did not proceed beyond these angles. The compounds $[RuCl(R)(CO)(PPh_3)_2]$ (R = Ph,[17] CH=CHPh[18]) were prepared according to published procedures. All other reagents were obtained from commercial sources.

Synthesis of [Ru(CO)(PMe$_2$Ph){B(mt)$_3$}](1f). *Method 1:* To a solution of $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ (**1a**: 0.50 g, 0.68 mmol) in dichloromethane (50 mL) was added an excess of PMe_2Ph (0.12 g, 0.12 mL, 0.87 mmol) under an inert atmosphere. The mixture was stirred for 1 hour and then the solvent was reduced and a yellow precipitate was formed on addition of ethanol (20 mL). The product was isolated by filtration, washed with ethanol (2 x 10 mL) and hexane (10 mL) and dried in vacuo. Yield = 0.31 g (0.51 mmol, 74%). *Method 2:* A mixture of $[Ru(CH=CHPh)Cl(CO)(PMe_2Ph)_3]$ (**3**: 0.41 g, 0.60 mmol) and $Na[HB(mt)_3]$ (0.23 g, 0.61 mmol) was heated under reflux in THF (30 mL) for 12 hours. The mixture was allowed to cool and then filtered. The filtrate was concentrated under reduced pressure (*ca* 5 mL) and then diluted with hexane (20 mL) resulting in the formation of a yellow precipitate. The product was filtered off and washed with diethyl ether (2 x 20 mL) and further recrystallised from a mixture of CH_2Cl_2 and ethanol. The resulting product was washed with petroleum ether (60-80°C) (20 mL) and then diethyl ether (10 mL) dried in vacuo. Yield = 0.19 g (0.31 mmol, 51%). [NB: The reaction does not proceed to completion at room temperature]. IR (cm^{-1}) Nujol: 1883 ν_{CO}, 1552w, 1181s, 1041m, 937m, 897m. ATR: 3115, 2970, 1882 ν_{CO}. CH_2Cl_2: 1887 ν_{CO}. ^{1}H NMR (300.7 MHz, $CDCl_3$): δ_H = 2.01 (d, 6 H, $^2J_{PH}$ = 5, PCH_3), 3.65 (s, 6 H, NCH_3), 3.73 (s, 3 H, NCH_3), 6.14, 6.39 (d x 2, 2 H x 2, $^3J_{HH}$ = 1.9, NCH=CHN), 6.48, 6.70 (d x 2, 1 H x 2, $^3J_{HH}$ = 1.9 Hz, NCH=CHN), 7.11, 7.24, 7.54 (m x 3, 5 H, C_6H_5). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$): δ_C = 18.40 (d, $^1J_{PC}$ = 15.4, PCH_3), 33.7 (2C, NCH_3), 34.2 (1C, NCH_3), 116.3, 117.4 (NCH=CHN), 120.8, 122.1 [$C^4(C_6H_5)$], 127.9 [d, $^3J_{PC}$ = 4.6, $C^{3,5}(C_6H_5)$], 128.0 [$C^4(C_6H_5)$], 130.3 [d, $^2J_{PC}$ = 12.8, $C^{2,6}(C_6H_5)$], 142.3 [d, $^1J_{PC}$ = 19.8, $C^1(C_6H_5)$], 170.9 (1C, CS), 171.1 (2C, CS), 206.5 (RuCO). $^{13}C\{^1H\}$ (176 MHz, $CDCl_3$): δ_C 18.6 (d, $^1J_{PC}$ = 15.8, PCH_3), 33.7, 34.2 (NCH-3), 116.5 (d, $^4J_{PC}$ = 2.3, NCH=CHN), 116.6 (d, $^4J_{PC}$ = 1.7, NCH=CHN), 122.2 [$C_4(C_6H_5)$], 128.0, 128.1 (NCH=CHN), 128.0 [d, $^3J_{PC}$ = 7.9, $C^{3,5}(C_6H_5)$], 130.3 [d, $^2J_{PC}$ = 12.3, $C^{2,6}(C_6H_5)$], 142.2 [d, $^1J_{PC}$ = 19.4, $C^1(C_6H_5)$], 166.8 (d, $^3J_{PC}$ = 22.9, CS), 170.1 (d, $^3J_{PC}$ =

17.6, CS), 206.7 (d, $^2J_{PC}$ = 5.3 Hz, CO). $^{31}P\{^1H\}$ NMR (283 MHz, $CDCl_3$): δ_P = –13.3 (br s). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B = 15.4 (br s). FAB-MS: *m/z* (%): 619(25) $[M]^+$, 591(10%)$[M\text{-}CO]^+$, 452(40%)$[M\text{-}CO\text{-}PMe_2Ph]^+$. ESI-MS (+) m/z: 618.0 $[M]^+$. Accurate mass: Found 618.0201 $[M]^+$, Calcd. for $C_{21}H_{26}{}^{11}BN_6OPS_3{}^{102}Ru$ 618.0204; Found 641.0121 $[M+Na]^+$, Calcd. for $C_{21}H_{26}{}^{11}BN_6O^{23}NaPS_3{}^{102}Ru$ 641.0102; Found 1258.0226 $[M–H+Na]^+$. Calcd. for $C_{42}H_{51}{}^{11}B_2N_{12}O_2{}^{23}NaP_2S_6{}^{102}Ru_2$ 1258.0228. Anal. Found: C, 40.91; H, 4.18; N, 13.49%. Calcd. for $C_{21}H_{26}BN_6OPRuS_3$: C, 40.85; H, 4.24; N, 13.61%.

Crystals suitable for crystallographic analysis were obtained from slow evaporation of a concentrated solution in dichloromethane/n-pentane over one day. *Crystal data for* $C_{21}H_{26}BN_6OPRuS_3$: M_w = 617.53, monoclinic, $P2_1/c$, a = 14.4644(2), b = 14.2915(2), c = 13.0253(1) Å, β = 102.2830(13)°, V = 2630.93(2) Å^3, Z = 4, $D_{calcd.}$ = 1.559 Mg m^{-3}, μ(Cu Kα) = 7.84 mm^{-1}, T = 150(2) K, yellow block, 0.39 x 0.19 x 0.09 mm, 5,301 independent reflections. F^2 refinement, R_1 = 0.035, wR_2 = 0.095 for 4,954 reflections ($I > 2.0\sigma(I)$, $2\theta_{max}$ = 144º), 307 parameters, 42 restraints, CCDC 1874175.

Synthesis of [Ru(CO)(PCy$_3$){B(mt)$_3$}] (1g). A mixture of $[RuCl(Ph)Cl(CO)(PCy_3)_2]$ (**4**: 0.50 g, 0.62 mmol) and Na[HB(mt)$_3$] (0.23 g, 0.62 mmol) was stirred in CH_2Cl_2 (30 mL) for 2 hours. The clear yellow solution was filtered through diatomaceous earth and the solvent volume of the filtrate was reduced to *ca* 5 mL. Hexane (20 mL) was added and the total volume reduced slowly to provide a pale yellow precipitate. The product was isolated by filtration and recrystallised from a mixture of CH_2Cl_2 and ethanol, isolated by filtration, washed with diethyl ether (20 mL) and dried *in vacuo*. Yield = 0.36 g (77%). IR (cm^{-1}) Nujol: 1872 ν_{CO}, 1554w, 1181vs, 1090m 920w. CH_2Cl_2: 1876 ν_{CO}. ATR: 2923w, 2847w, 1871 ν_{CO}. ^1H NMR (300.7 MHz, $CDCl_3$): δ_H = 1.23 - 2.05 (m.br., 33 H, C_6H_{11}), 3.46 (s, 6 H, NCH_3), 3.50 (s, 3 H, NCH_3), 6.33, 6.48 (d x 2, 2 H, $^3J_{HH}$ = 1.8, NCH=CHN), 6.66, 6.93 (d x 2, $^3J_{HH}$ = 2.0 Hz, 4H, NCH=CHN) ppm. ^1H NMR (700 MHz, $CDCl_3$): δ_H = 1.30 – 2.07 (sets of m, 33 H, C_6H_{11}), 3.46 (s, 3 H, NCH_3), 3.48 (s, 6 H, NCH_3), 6.37 (d, 1 H, $^3J_{HH}$ = 2.1, NCH=CHN), 6.50 (d, 1 H, $^3J_{HH}$ = 1.7, NCH=CHN), 6.70 (d, 2 H, $^3J_{HH}$ = 1.8, NCH=CHN), 6.99 (d, 1 H, $^3J_{HH}$ = 2.0, NCH=CHN). $^{13}C\{^1H\}$ APT NMR (100 MHz, $CDCl_3$): δ_C = 26.9 $[CH_2(C_6H_{11})]$, 28.1 [d, $^2J_{PC}$ = 9.4, $CH_2(C_6H_{11})$], 29.9 [d, $^2J_{PC}$ = 2.2, $CH_2(C_6H_{11})$], 33.9, 34.4 (NCH_3), 35.3 [d, $^1J_{PC}$ = 6.3, $PCH(C_6H_{11})$], 116.3 (d, $^4J_{PC}$ = 1.8, NCH=CHN), 116.5 (d, $^4J_{PC}$ = 1.2, NCH=CHN), 121.9, 122.0 (NCH=CHN), 166.8 (d, $^3J_{PC}$ = 17.8, CS), 171.0 (d, $^3J_{PC}$ = 13.5 Hz, CS), 208.2 (CO). $^{31}P\{^1H\}$ NMR (283 MHz, $CDCl_3$): δ_P = 28.2 (br s). $^{11}B\{^1H\}$ NMR (128 MHz, $CDCl_3$): δ_B = 15.4 (br s). ESI-MS (+) *m/z*: 760.2 $[M]^+$, 783.2 $[M+Na]^+$. Accurate mass: Found 760.1951 $[M]^+$, Calcd. for $C_{31}H_{48}{}^{11}BN_6OPS_3{}^{102}Ru$ 760.1926. Found 783.1813 $[M+Na]^+$, Calcd. for $C_{31}H_{48}{}^{11}BN_6O^{23}NaPS_3{}^{102}Ru$ 783.1824. Anal. Found: C, 49.24; H, 6.36; N, 11.16%. Calcd. for $C_{31}H_{48}BN_6OPS_3Ru$: C, 49.00; H, 6.37; N, 11.06%. Crystals suitable for crystallographic analysis were obtained from slow evaporation of a concentrated solution in dichloromethane/n-pentane over one day. *Crystal data for* $C_{31}H_{48}BN_6OPRuS_3.CH_2Cl_2$ (150 K): *Mw* = 844.75, triclinic, *P*-1 (No. 2), a = 11.5008(5), b = 12.1448(5), c = 14.2700(4) Å, α = 82.893(3), β = 81.948(3), γ = 75.012(4)°, V = 1898.38(5) Å^3, Z = 2, $D_{calcd.}$ = 1.478 Mgm^{-3}, μ(Cu Kα) = 6.86 mm^{-1}, T = 150(2) K, colourless needle, 0.28 x 0.06 x 0.04 mm, 7,649 independent reflections, F^2 refinement, R_1 = 0.041, wR_2 = 0.106 for 6,878 reflections ($I > 2.0\sigma(I)$, $2\theta_{max.}$ = 144°), 442 parameters, 0 restraints CCDC 1874176.

Synthesis of [Ru(CO)(PMe$_3$){B(mt)$_3$}] (1h) – A solution of $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ (**1a**: 1.005 g, 1.36 mmol) in CH_2Cl_2 (20 mL) was treated with a solution of PMe_3 (0.12 g, 1.50 mmol) in THF (10mL) and the mixture stirred for 16 hours. Diethyl ether (40 mL) was added to provide a pale yellow precipitate which was freed of supernatant by cannula filtration. The residue was recrystallised from a mixture of dichloromethane and ethanol. Yield 0.625g (1.12 mmol, 83%). IR (cm^{-1}) Nujol: 1993 ν_{CO}, 1554w, 1181s, 944.9m. IR (cm^{-1}) CH_2Cl_2: 1885 ν_{CO}. ^1H NMR (270 MHz, $CDCl_3$); δ = 1.43 (d, 9 H, $^2J_{PH}$ = 5.4 Hz, PCH_3) 3.42 (s, 3 H; NCH3), 3.43 (s, 6 H, NCH3), 6.36, 6.54 (d x 2, 1 H x 2, $^3J_{HH}$ not resolved, NHC=CHN), 6.70, 6.96 (d x 2, 2 H x 2, $^3J_{HH}$ not resolved, NHC=CHN) ppm. $^{13}C\{^1H\}$ NMR (67.9 MHz, $CDCl_3$): δ_C = 19.51 (d, $^1J_{PC}$ = 15.5, PCH_3), 33.7, 34.2 (NCH_3), 116.5, 122.1 (NCHCHN), 171.3, 171.6 (CS), 206.9 (RuCO). $^{31}P\{^1H\}$ NMR (72.9 Hz, $CDCl_3$): δ_P = –25.2 (s.br.). $^{11}B\{^1H\}$ NMR (86.6 MHz, $CDCl_3$): δ_B = 14.6 (br.). LR-FAB-MS (nba matrix): *m/z* = 556(12) $[M]^+$, 528(29) $[M\text{-}CO]^+$, 452(53) $[M\text{-}CO\text{-}PMe_3]^+$. Anal. Found; C, 34.23; H, 4.59; N, 14.88%. Calc. for $C_{16}H_{24}BN_6OPRuS_3$: C, 34.58; H, 4.36; N, 15.13%: Crystals suitable for crystallographic analysis were obtained from slow evaporation of a concentrated solution in dichloromethane/n-pentane. *Crystal data for* **1h**: $C_{16}H_{24}BN_6OPRuS_3$, M_w = 555.44, monoclinic, $P2_1/c$ (no. 14), a = 13.763(2), b = 12.5156(18), c = 13.792(3) Å, β = 95.727(14)°, V = 2364.0(7) Å^3, Z = 4, $D_{calcd.}$ = 1.561 Mg m^{-3}, μ(Mo-Kα) = 1.016 mm^{-1}, T = 293 K, yellow prisms, 3,079 independent measured reflections (R_{int} = 0.0333), F^2 refinement, R_1 = 0.0390, wR_2 = 0.0871, 2,362 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, completeness to θ_{full}(22.5°) = 100.0%], 295 parameters. CCDC 1874177. The trimethyl phosphine group in the structure of **1h** was found to be disordered. Three orientations were identified of *ca*. 46, 32 and 22% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the three partial occupancy phosphorus atoms were refined anisotropically (the carbon and hydrogen atoms of all three orientations were refined isotropically).

Synthesis of [Ru(CO){P(OMe)$_3$}{B(mt)$_3$}] (1i). *Method 1:* A mixture of $[Ru(CO)(PPh_3)\{B(mt)_3\}]$ (**1a**: 0.500 g, 0.675 mmol) and $P(OMe)_3$ (0.08 mL, 0.72 mmol) was heated under reflux in hexane (30 mL) for 16 hrs, during which time a colour change from yellow to orange was observed. The solvent was reduced and petroleum spirit added (80-100°C, 20 mL). The solvent volume was further reduced to yield an off-white precipitate. The solid was filtered off, washed with petroleum spirit (60-80°C, 2 x 20 mL) and dried in vacuo. Yield = 0.27 g (0.45 mmol, 62%). *Method 2:* A mixture of $[Ru(CH{=}CHPh)Cl(CO)\{P(OMe)_3\}_3]$ (5: 0.23 g, 0.36 mmol) and Na[HB(mt)$_3$] (0.14 g, 0.36 mmol) was heated under reflux in THF (30 mL) for 12 hours. The mixture was allowed to cool and the clear yellow solution was filtered through diatomaceous earth. The filtrate was concentrated under reduced pressure to *ca* 5 mL and then hexane added (20 mL). The total volume was further reduced and the resulting yellow precipitate was allowed to settle and the mother-liquor

decanted off. The remaining solid was washed with petroleum-ether (60-80°C, 20 mL) and diethyl-ether (10 mL) and then dried in vacuo. Yield = 0.130 g (0.22 mmol, 59%). NB: This resulting solid is susceptible to forming a gum when the THF solvent is not completely removed during the work-up process. *Method 3:* A solution of [Ru(CO)(PPh$_3$){B(mt)$_3$}] (**1a**: 0.202 g, 0.27 mmol) and P(OMe)$_3$ (0.20 mL, 1.64 mmol) in THF (20 mL) was heated under reflux for 16h. The bright yellow precipitate was separated from the supernatant by cannula filtration, washed with n-pentane and dried *in vacuo*. Yield: 0.080 g (0.133 mmol, 49%). IR (cm^{-1}) CH_2Cl_2: 1907 ν_{CO}. Nujol: 1883 ν_{CO}, 1552w, 1181s, 1041m, 937m, 897m. ATR: 3164w, 3114w, 1894 ν_{CO}, 1556m, 1184s, 1011v. ^{1}H NMR (300.7 MHz, $CDCl_3$) δ_H = 3.72 (s, 6 H, NCH_3), 3.73 (s, 3 H, NCH_3), 3.92 (d, $^3J_{PH}$ = 11.5, 9 H, OCH_3), 6.34, 6.57 (d x 2, $^3J_{HH}$ = 1.8, 2 H, NCH=CHN), 6.64, 6.72 (d x 2, 2 H $^3J_{HH}$ = 1.8, NCH=CHN), 7.00, 7.25 (d x 2, 2 H, $^3J_{HH}$ = 2.0 Hz, NCH=CHN) ppm. ^{13}C{^{1}H} NMR (176 MHz, $CDCl_3$): δ_C = 33.8, 34.3 (NCH_3), 50.8 (OCH_3), 116.6 (d, $^4J_{PC}$ = 3.2, NCH=CHN), 116.7 (d, $^4J_{CP}$ = 2.6, NCH=CHN), 122.5, 122.7 (NCH=CHN), 167.3 (d, $^3J_{PC}$ = 27.2, CS), 171.0 (d, $^3J_{PC}$ = 22.1, CS), 206.0 (d, $^2J_{PC}$ = 7.1 Hz, CO). ^{31}P{^{1}H} NMR (283 MHz, $CDCl_3$): δ_P = 159.1 (br s). ^{11}B{^{1}H} NMR (128 MHz, $CDCl_3$): δ_B = 14.5 (br s). LR FAB-MS (nba): *m/z* (%) = 603(15) [M]$^+$, 575(19) [M-CO)]$^+$, 452(44) [M-CO-P(OMe)$_3$]$^+$. ESI-MS (+) m/z: 604.0 [HM]$^+$, 627.0 [M + Na]$^+$. Accurate mass: Found 603.9898 [M]$^+$, Calcd. for $C_{16}H_{24}{}^{11}BN_6O_4PS_3{}^{102}Ru$ 603.9895. Found 626.9792 [M+Na]$^+$, Calcd. for $C_{16}H_{24}{}^{11}BN_6O_4{}^{23}NaPS_3{}^{102}Ru$ 626.9793. Found 1230.9668 [2M+Na]$^+$, Calcd. for $C_{32}H_{48}{}^{11}B_2N_{12}O_8{}^{23}NaP_2S_6{}^{102}Ru_2$ 1230.9688. Anal. Found; C 31.94; H, 4.12; N, 13.84%. Calcd. For $C_{16}H_{24}O_4N_6BPRuS_3$; C, 31.85; H, 4.01; N, 13.93%:

Synthesis of [Ru(CO){P(OEt)$_3$}{B(mt)$_3$}] (1j) – As described for **1i** above (Method 1, **1a**: 1.005 g, 1.36 mmol). Yield 0.756 g (1.17 mmol, 86%). IR (cm^{-1}) Nujol: 1898 ν_{CO}, 1553w, 1179s, 1030s, 921m. IR (cm^{-1}) CH_2Cl_2: 1904 ν_{CO}. ^{1}H NMR (270 MHz, $CDCl_3$); δ = 1.30 (dt, 9 H, 2JHH = 7.1, $^4J_{PH}$ = 0.8, CCH_3), 3.46 (s, 9 H; NCH_3), 4.03 (dq, 6 H, $^3J_{PH}$ ~ $^3J_{HH}$ = 7.1, OCH_2), 6.34, 6.54 (d x 2, 1 H x 2, $^3J_{HH}$ = 1.8 Hz, NHC=CHN), 6.69, 6.93 (s x 2, 2 H x 2, $^3J_{HH}$ not resolved, NHC=CHN) ppm. ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$): δ_C = 16.8 (d, $^3J_{PC}$ = 6.1, CCH_3), 33.7(2C), 34.3 (1C, NCH_3), 59.31 (OCH_2), 116.6 (3C), 122.4(1C), 122.5(2C, NCHCHN), 170 (br., CS, onset of fluxionality). ^{31}P{^{1}H} NMR (72.9 Hz, $CDCl_3$): δ_P = 156.7 (s.br.). ^{11}B{^{1}H} NMR (86.6 MHz, $CDCl_3$): δ_B = 14.0 (br.). LR-FAB-MS (nba matrix): *m/z* = 646(18) [M]$^+$, 618(32) [M-CO]$^+$, 480(3) [M-P(OEt)$_3$]$^+$, 452(100)[M-CO-P(OEt)$_3$]$^+$. Anal. Found; C, 34.12; H, 4.93; N, 12.92%. Calc. for $C_{19}H_{30}BN_6O_4PRuS_3$: C, 34.34; H, 4.69; N, 13.02%. *Crystal data for* **1j**: $C_{19}H_{30}BN_6O_4PRuS_3$, M_w = 645.52, orthorhombic, *Pbca* (no. 61), *a* = 13.3878(11), *b* = 16.5415(9), *c* = 25.3837(14) Å, *V* = 5621.3(6) Å^3, *Z* = 8, $D_{calcd.}$ = 1.525 Mg m^{-3}, μ(Cu-Kα) = 7.445 mm^{-1}, *T* = 293 K, yellow prisms, 4,170 independent measured reflections (R_{int} = 0.0656), F^2 refinement, R_1 = 0.0532, wR_2 = 0.1470, 3,276 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], completeness to θ_{full}(60.0°) = 100.0%], 365 parameters. CCDC 1874178. The triethyl phosphite group in the structure of **1j** was found to be disordered. Two orientations were identified of *ca* 68 and 32% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the two partial occupancy phosphorus atoms and the carbon atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically).

Synthesis of [Ru(CO){P(OPh)$_3$}{B(mt)$_3$}] (1k) – As described for **1i** above (Method 1, **1a**: 1.000 g, 1.35 mmol). Yield 0.937 g (1.19 mmol, 88%). IR (cm^{-1}) Nujol: 1923 ν_{CO}, 1590w, 1185s, 901m, 871m. IR (cm^{-1}) CH_2Cl_2: 1923 ν_{CO}. ^{1}H NMR (270 MHz, $CDCl_3$); δ = 3.37 (s, 6 H; NCH_3), 3.40 (s, 3 H, NCH=CHN), 6.35, 6.61 (d x 2, 1 H x 2, $^3J_{HH}$ = 1.8 Hz, NHC=CHN), 6.73, 6.93 (d 2 , 2 H x 2, $^3J_{HH}$ not resolved, NHC=CHN), 7.05-7.15, 7.23 – 7.31 (m x 2, 15 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR (67.9 MHz, $CDCl_3$): δ_C = 33.6(2C), 34.0 (1C, NCH_3), 116.6 (3C), 121.7 [d, 3JPC = 4.3, $C^{2,6}(C_6H_5)$], 122.5(2C), 122.7(1C, NCHCHN), 123.6 [$C^4(C_6H_5)$], 129.2 [$C^{3,5}(C_6H_5)$], 152.4 [d, $^2J_{PC}$ = 5.4, $C^1(C_6H_5)$], 170.2, 170.5 (CS). ^{31}P{^{1}H} NMR (72.9 Hz, $CDCl_3$): δ_P = 136.5 (s.br.). ^{11}B{^{1}H} NMR (86.6 MHz, $CDCl_3$): δ_B = 13.0 (br.). LR-FAB-MS (nba matrix): *m/z* = 790(71) [M]$^+$, 762(26) [M-CO]$^+$, 452(70)[M-CO-P(OPh)$_3$]$^+$. Anal. Found; C, 47.01; H, 3.94; N, 10.92%. Calcd. for $C_{31}H_{30}BN_6O_4PRuS_3$: C, 47.14; H, 3.83; N, 10.65%.

Crystals of a dichloromethane solvate **1k**.2CH_2Cl_2 suitable for crystallographic analysis were obtained from slow evaporation of a concentrated solution in dichloromethane/hexane. *Crystal data for* **1k**.2CH_2Cl_2: $C_{31}H_{30}BN_6O_4PRuS_3{\cdot}2(CH_2Cl_2)$, M_w = 959.49, triclinic, *P*-1 (no. 2), *a* = 11.8771(4), *b* = 12.3847(4), *c* = 16.6567(5) Å, α = 93.569(2), β = 108.863(3), γ = 114.826(2)°, *V* = 2047.58(12) Å^3, *Z* = 2, $D_{calcd.}$ = 1.556 Mg m^{-3}, μ(Cu-Kα) = 7.671 mm^{-1}, *T* = 293 K, pale yellow platy needles, 5,612 independent measured reflections (R_{int} = 0.0528), F^2 refinement, R_1 = 0.0501, wR_2 = 0.1345, 4,828 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$], completeness to θ_{full}(60.0°) = 92.3%], 504 parameters. CCDC 1874179. The triphenylphosphite group in the structure of **1k** was found to be disordered. Two orientations were identified of *ca*. 79 and 21% occupancy, their geometries were optimized, the thermal parameters of adjacent atoms were restrained to be similar, and only the two partial occupancy phosphorus atoms and the carbon atoms of the major occupancy orientation were refined anisotropically (the rest were refined isotropically).

Synthesis of *mer*-[Ru(CH=CHPh)Cl(CO)(PMe$_2$Ph)$_3$] (3) - A mixture of [Ru(CH=CHPh)Cl(CO)(PPh$_3$)$_2$] (1.00 g, 1.30 mmol) and three equivalents of dimethylphenylphosphine (0.54 mL, 0.52 g, 3.80 mmol) was stirred in CH_2Cl_2 (50 mL) for 1 hour. The solvent volume was reduced under reduced pressure and ethanol (20 mL) added to precipitate the white crystalline product. The precipitate was filtered off and washed with ethanol (20 mL) and hexane (10 mL). Yield = 0.68 g (79%). IR (cm^{-1}) Nujol: 1919 ν_{CO}. CH_2Cl_2: 1918 ν_{CO}. ^{1}H NMR (300.7 MHz, $CDCl_3$): δ_H = 1.09 (d, $^2J_{PH}$ = 7.2, 6 H, *cis*-PMe$_2$Ph), 1.48 (t^v, J_{PH} = 6.4, 6 H, *trans*-PMe$_2$), 1.62 (t^v, 6 H, J_{PH} = 4.92 Hz, *trans*-PMe$_2$), 6.70 (dd, 1 H, CH_βPh, not resolved), 8.35 (ddt, 1 H, $RuCH_\alpha$), 7.08 – 7.49 (m, 20 H, C_6H_5) ppm. ^{13}C{^{1}H} NMR (75.4 MHz, $CDCl_3$): δ_C = 203.9 (dt, not resolved, RuCO), 163.7 [$C^1(C_6H_5)$], 140.0 [$C^{2,6}(C_6H_5)$], 128.7 [$C^{3,5}(C_6H_5)$], 124.4 [$C^4(C_6H_5)$], 14.38 (PCH_3) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ_P = –8.80 (t, $^2J_{PP}$ = 23.1, 1 P, *cis*-PMe$_2$Ph), –1.17 [d, $^2J_{PP}$ = 23.1 Hz, 2 P, *trans*-(PMe$_2$Ph)$_2$] ppm. FAB-MS *m/z* (%): 681(10) [M]$^+$, 579(40) [M-HCCHPh]$^+$, 544(35) [M-Cl-HCCHPh]$^+$, 516(55) [M-CO-Cl-HCCHPh]$^+$, 377(100) [Ru(PMe$_2$Ph)$_2$]$^+$. Anal. Found: C, 58.37; H, 6.02%. Calcd. for

$C_{33}H_{40}ClOP_3Ru$: C, 58.09; H, 5.91%. Single crystals suitable for *X*-ray crystallography were obtained by layering pentane upon a CH_2Cl_2 solution of the complex. *Crystal data:* $C_{33}H_{40}ClOP_3Ru$; M_r = 682.127, monoclinic, $P2_1/c$, a = 15.3727(2), b = 12.4583(2), c = 17.6126 (3) Å, β = 105.0989(7)°, V = 3256.68(9) Å^3, Z = 4; $D_{calcd.}$ = 1.391 Mgm^{-3}, μ (Mo-Kα) = 0.74 mm^{-1}, T = 200(2) K, yellow prism 0.26 x 0.16 x 0.14 mm, 7,457 independent measured reflections, F refinement, R_1 = 0.031, wR_2 = 0.038, 4,016 independent observed absorption corrected reflections [$I > 3\sigma(I)$, $2\theta \leq 55°$], 353 parameters.

Synthesis of [RuCl(Ph)(CO)(PCy_3)$_2$] (4). A mixture of [RuCl(Ph)(Cl)(CO)(PPh_3)$_2$] (3.00 g, 3.92 mmol) and PCy_3 (3.37 g, 12.0 mmol) was dissolved THF (40 mL) and heated under reflux in a N_2 atmosphere for 4 hours. The solution was allowed to cool to room temperature and then diluted with ethanol (40 mL) and concentrated to a minimum under reduced pressure to provide a red microcrystalline precipitate which was isolated by filtration. The product was washed with ethanol (2 x 20 mL), dried *in vacuo* and stored under an oxygen- and moisture-free atmosphere. Yield = 2.52 g (3.13 mmol, 80%). IR (cm^{-1}) Nujol: 1897 ν_{CO}. CH_2Cl_2: 1901 ν_{CO}. ^{1}H NMR (300.7 MHz, $CDCl_3$): δ_H = 1.16 – 1.72 (m.br, 66 H, C_6H_{11}), 6.58 – 6.61, 7.24 - 7.68 (m, 5 H, C_6H_5) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, $CDCl_3$): δ_P = 24.8. FAB-MS: *m/z* (%) 805.2(10)[M]$^+$, 767.1(100)[M-Cl]$^+$. Anal. Found: C, 63.91; H, 9.14%. Calcd. for $C_{43}H_{71}ClOP_2Ru$: C, 64.36; H, 8.92%. This complex with comparable spectroscopic data, has previously been obtained via the adventitious hydrolysis of Grubbs' catalyst [Ru(=CHPh)Cl_2(PCy_3)$_2$].[19]

Synthesis of [Ru(CH=CHPh)Cl(CO){P(OMe)$_3$}$_3$] (5) - A mixture of [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] (0.55 g, 0.60 mmol) and three equivalents of $P(OMe)_3$ (0.21 mL, 1.8 mmol) was heated under reflux in hexane (50 mL) for 16 hours during which time the colour faded from red to colourless. The solution was allowed to cool and the solvent removed *in vacuo*. The white product was recrystallised from CH_2Cl_2 (10 mL) and petroleum spirit (10 mL). This is a very soluble compound, which compromises the isolated yield though the reaction is spectroscopically quantitative. Yield = 0.23 g (59%). IR (cm^{-1}) Nujol: 1969 ν_{CO}. CH_2Cl_2: 1969 ν_{CO}. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6): δ_P = 128.9 [d, $^2J_{AB}$ = 42.3, 2 P, *trans*-$P(OMe)_3$], 142.4 [t, $^2J_{AB}$ = 43.0 Hz, 1 P, *cis*-$P(OMe)_3$] ppm. FAB-MS: *m/z* (%): 639.9(3)[M]$^+$, 607.0(4)[M-Cl]$^+$, 583.7(20)[M-CO-Cl]$^+$. Anal. Found C,33.81; H, 5.18%. Calc. for $C_{18}H_{34}O_4ClP_3Ru$: C, 33.78; H, 5.32%.

Synthesis of [Ru(CH=CHPh)Cl(CO){P(OMe)$_3$}(PPh$_3$)$_2$] (6) - To a solution of [Ru(CH=CHPh)Cl(CO)(PPh_3)$_2$] (0.55 g, 0.60 mmol) in CH_2Cl_2 (60 mL) was added $P(OMe)_3$ (0.25 cm^3, 1.8 mmol). The mixture was stirred at room temperature and an instant colour change from red to light yellow was observed, however the reaction was left to stir for further two hours. The CH_2Cl_2 solvent was reduced to a minimum (*ca* 10 mL) and ethanol (20 mL) added and the total volume further reduced slowly under reduced pressure to provide an off-white precipitate of the desired complex. Yield = 0.82 g (42%). IR (cm^{-1}) Nujol: 1955 ν_{CO}. ^{1}H NMR (300.7 MHz, C_6D_6): δ_H = 3.32 (d, 9 H, $^3J_{PH}$ = 10.1, $POCH_3$), 5.70 (dd, 1 H, $CH_\beta Ph$), 8.35 (m=ddt, not resolved, 1 H, $RuCH_\alpha$), 7.24-7.26, 7.74-7.80 (m, 35 H, C_6H_5) ppm. ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6); δ_P = 127.7 [t, $^2J_{PP}$ = 43.6, $P(OMe)_3$], 22.6 [d, $^2J_{PP}$ = 43.6 Hz, 2 P, *trans*-PPh_3] ppm. Anal. Found: C, 63.21; H, 5.36%. Calcd. for $C_{48}H_{46}ClO_4P_3Ru$: C, 62.90; H, 5.06%.

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