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Alkenyl and alkynyl complexes of osmium(II) derived from $[OsH(Cl)(CO)(BTD)(PPh_3)_2]$ (BTD = 2,1,3-benzothiadiazole)

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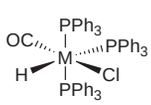
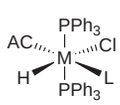
Treatment of $[OsH(CA)(NCMe)_2(PPh_3)_2]^+$ (A = O or S) with $[NEt_4]Cl$ and 2,1,3-benzothiadiazole (BTD) provided $[OsH(Cl)(CA)(BTD)(PPh_3)_2]$ (A = O or S). Under mild conditions, the complex $[OsH(Cl)(CO)(BTD)(PPh_3)_2]$ hydroosmiates ethynyltoluene, ethyne and di(4-tolyl)butadiyne to provide vinyl complexes $[Os(CH{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ (R = C_6H_4Me-4), $[Os(CH{=}CH_2)Cl(CO)(BTD)(PPh_3)_2]$ and $[Os\{C(C{\equiv}CR){=}CHR\}Cl(CO)(BTD)(PPh_3)_2]$. Complex $[OsH(CO)(NCMe)_2(PPh_3)_2]^+$ reacted with HC≡CR to provide $[Os(CH{=}CHR)(CO)(NCMe)_2(PPh_3)_2]^+$ which is converted by $[NEt_4]Cl$ into $[Os(CH{=}CHR)Cl(CO)(NCMe)(PPh_3)_2]$. Treatment of $[Os(CH{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ with $CNCMe_3$ or CO provided $[Os(CH{=}CHR)Cl(CO)(L)(PPh_3)_2]$ (L = $CNCMe_3$ or CO). The dithiocarbamate complex $[Os(CH{=}CHR)(S_2CNMe_2)(CO)(PPh_3)_2]$ and the osmatetraborane $[Os(CH{=}CHR)(B_3H_8)(CO)(PPh_3)_2]$ resulted from the reactions of $[Os(CH{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ with $Na[S_2CNMe_2]$ and $[NBu^n_4][B_3H_8]$, respectively, whereas with $K[HB(pz)_3]$ (pz = pyrazolyl) initially $[Os(CH{=}CHR)(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ was formed which is converted into $[Os(CH{=}CHR)(CO)(PPh_3)\{HB(pz)_3\}]$ on heating. No intermediates are however observed in the corresponding reaction with 1,4,7-trithiacyclononane ([9]aneS$_3$) to provide $[Os(CH{=}CHR)(CO)(PPh_3)([9]aneS_3)]^+$. The alkynyl complex $[Os(C{\equiv}CR)Cl(CO)(BTD)(PPh_3)_2]$ was obtained from either (i) the reaction of $[OsH(Cl)(CO)(BTD)(PPh_3)_2]$ with $[Hg(C{\equiv}CR)_2]$ or (ii) $[Os(CH{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ with an excess of HC≡CR. Treatment of $[Os(C{\equiv}CR)Cl(CO)(BTD)(PPh_3)_2]$ with $Na[S_2CNMe_2]$ or alternatively $[Os(CH{=}CHR)(S_2CNMe_2)(CO)(PPh_3)_2]$ with an excess of HC≡CR provided $[Os(C{\equiv}CR)(S_2CNMe_2)(CO)(PPh_3)_2]$, which can also be obtained from $[OsH(S_2CNMe_2)(CO)(PPh_3)_2]$ and $[Hg(C{\equiv}CR)_2]$. The BTD in $[Os(C{\equiv}CR)Cl(CO)(BTD)(PPh_3)_2]$ is substituted by $CNCMe_3$ to provide $[Os(C{\equiv}CR)Cl(CO)(CNCMe_3)(PPh_3)_2]$. The reaction of $[OsH(Cl)(CS)(BTD)(PPh_3)_2]$ with HC≡CR provided $[Os(CH{=}CHR)Cl(CS)(BTD)(PPh_3)_2]$ which in contrast to $[Os(CH{=}CHR)Cl(CO)(BTD)(PPh_3)_2]$ reacts with carbon monoxide to provide the thiocinnamoyl complex $[Os(\eta^2\text{-}SCCH{=}CHR)Cl(CO)(PPh_3)_2]$.

Introduction

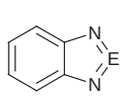
The hydrometallation of alkynes by hydrido complexes of osmium and ruthenium provides a facile entry into the chemistry of σ-vinyl complexes.[1] The readily accessible complex $[RuH(Cl)(CO)(PPh_3)_3]$ **1a**[2] has been shown to react with alkynes[3,4] and diynes[5] to provide co-ordinatively unsaturated σ-vinyl or σ-enynyl complexes which are themselves valuable precursors to a wide range of complexes bearing isocyanide,[6,7] poly(azolyl)borate,[8] triboronate,[9] and trithiacyclononane,[10] dithiocarbamate,[11] carboxylate[12] and phosphoniodithiocarboxylate[13] coligands. For many of these compounds the co-ordinatively saturated adducts $[Ru(CH{=}CHR)Cl(CO)(L)(PPh_3)_2]$ [L = 2,1,3-benzothiadiazole (BTD) or 2,1,3-benzoselenadiazole (BSD)] serve equally well as precursors by virtue of the lability of the heterocyclic ligands. These vinyl complexes result under mild conditions from the reactions of the hydrido complexes $[RuH(Cl)(CO)(L)(PPh_3)_2]$ (L = BTD **2a** or BSD **2b**)[14] with alkynes and alkynols.[15] Esteruelas, Oro and Werner[16] have developed an enormously rich chemistry based on the related complexes $[MH(Cl)(CO)(PPr^i_3)_2]$ (M = Ru or Os)[16] which are stable and highly reactive 16-electron species due to the steric encumbrance of the PPr^i_3 ligands which precludes the formation of tris(phosphine) complexes in contrast to the PPh_3 relatives. Whilst the PPr^i_3 class of complex allows the study of osmium σ-vinyl chemistry in parallel with that of ruthenium, the hydrometallation of alkynes by $[OsH(Cl)(CO)(PPh_3)_3]$ **1b** has met with very limited success. Roper and co-workers[17] have



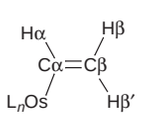
M = Ru **1a**
M = Os **1b**



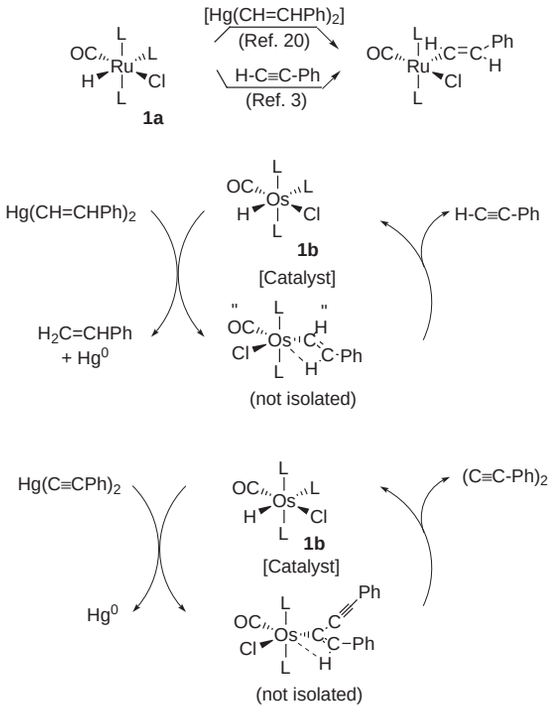
M = Ru, A = O, L = BTD **2a**
M = Ru, A = O, L = BSD **2b**
M = Os, A = O, L = BTD **2c**
M = Os, A = S, L = BTD **2d**



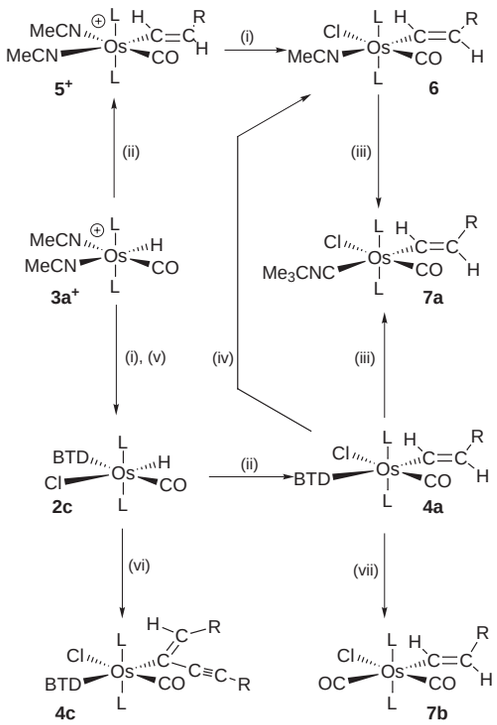
E = S (BTD)
E = Se (BSD)



described an unusual cyclotrimerisation process which occurs with ethyne, the initial stages of which are consistent with the intermediate formation of $[Os(CH{=}CH_2)Cl(CO)(PPh_3)_2]$. However, in general it appears in the equilibrium reaction with alkynes that the hydride precursor is preferred to the alkyne insertion product, in distinct contrast to the chemistry of ruthenium. This interpretation follows from two observations (Scheme 1): whilst the complex $[Ru(CH{=}CHPh)Cl(CO)(PPh_3)_2]$ may be obtained from the reaction of **1a** with either ethynylbenzene[3] or $[Hg(CH{=}CHPh)_2]$,[18] there is no apparent reaction between the osmium analogue **1b** and



Scheme 1 L = PPh_3.



Scheme 2 L = PPh_3, R = C_6H_4Me-4. *Reagents*: (i) $[Et_4N]Cl$; (ii) HC≡CR; (iii) $CNCMe_3$; (iv) MeCN; (v) BTD; (vi) RC≡C–C≡CR; (vii) CO.

ethynylbenzene. Furthermore, with $[Hg(CH=CHPh)_2]$ catalytic demercuriation occurs to regenerate **1b**, elemental mercury, and presumably styrene and ethynylbenzene. This is consistent with the formation of $[Os(CH=CHPh)Cl(CO)(PPh_3)_2]$ which under the reaction conditions (refluxing toluene) and in the presence of liberated PPh_3 undergoes β-Os–H elimination to generate ethynylbenzene and **1b**.[18] The second illustration comes from the reactions of **1** with $[Hg(C{\equiv}CPh)_2]$: in the case of ruthenium (**1a**) the product is the enynyl complex $[Ru\{C(C{\equiv}CPh){=}CHPh\}Cl(CO)(PPh_3)_2]$[19] which is also obtained from the reaction of **1a** with diphenylbutadiyne.[5] This complex catalyses the demercuriation of $[Hg(C{\equiv}CPh)_2]$ to provide elemental mercury and diphenylbutadiyne and may be recovered after the catalysis. Although **1b** will also catalyse this demercuriation, the organometallic product obtained after catalysis is the starting hydride complex **1b**, rather than an enynyl derivative (Scheme 1).[20]

The complex $[OsH(O_2CCF_3)(CO)(PPh_3)_2]$ has been shown to react with tolane (PhC≡CPh) to provide the *cis*-stilbenyl complex $[Os(CPh{=}CHPh)(O_2CCF_3)(CO)(PPh_3)_2]$.[21,22] This result, taken in combination with the above considerations, led us to conclude that the hiatus in the potential alkyne hydrometallation chemistry based on **1b** lies in (i) the competitive co-ordination of the third phosphine ligand and (ii) the inherent stability of **1b** relative to alkyne insertion products. We have therefore investigated the synthesis of the BTD complex $[OsH(Cl)(CO)(BTD)(PPh_3)_2]$ **2c**, and now show that a rich organometallic chemistry is indeed accessible from this species.

Results and discussion

Our initial attempt to prepare $[OsH(Cl)(CO)(BTD)(PPh_3)_2]$ **2c** in a manner analogous to the ruthenium example (**2a**) failed. Thus heating complex **1b** with an excess of BTD in refluxing tetrahydrofuran fails to provide pure **2c**. Rather, essentially independent of reaction duration, an equilibrium mixture of colourless **1b** and orange **2c** is obtained, further supporting the idea that phosphine competes effectively for co-ordination to osmium. An alternative approach was therefore developed to remove this competition. The salt $[OsH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ **3a**·ClO_4 is readily obtained *via* the reaction of **1b** with $AgClO_4{\cdot}H_2O$ in refluxing acetonitrile.[23] Heating **3a**·ClO_4 in refluxing ethanol with an excess of $[NEt_4]Cl$ and BTD provides high yields of the desired complex **2c**. This complex may be assumed on the basis of spectroscopic data to adopt the stereochemistry shown in Scheme 2, which has been previously established for the ruthenium analogue **2a**.[14] Thus the hydride ligand gives rise to a triplet resonance at δ −15.00 [J(PH) = 16.2 Hz] in the ^{1}H NMR spectrum, confirming that it is *cis* to two chemically equivalent phosphine ligands. Intense ν(OsH) and ν(CO) absorptions are visible in the solid state infrared spectrum (Nujol) at 1974 and 1905 cm^{-1}, respectively. The molecular composition is supported by positive ion FAB mass spectroscopy which displays no molecular ion but instead a $[M - BTD]^+$ fragment at m/z = 780. Facile loss of the BSD ligand in the FAB mass spectra is a common feature of BSD complexes.[14,15,24] Fragmentations are however also observed which involve retention of the BTD ligand, thereby confirming that it is co-ordinated in the complex.

Alkenyl complexes

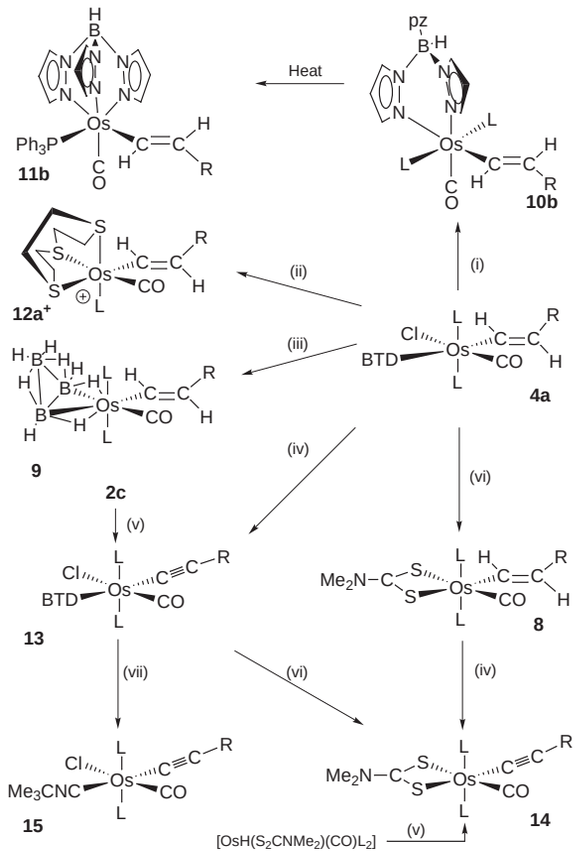
An instant deep purple coloration is observed on addition of 4-ethynyltoluene to a solution of complex **2c** in dichloromethane. A complex formulated as $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ **4a** may be isolated in high yield on addition of ethanol. No ν(OsH) absorption is observed in the infrared spectrum (Nujol), only an intense ν(CO) absorption at 1899 cm^{-1}. The species formed is confirmed as a vinyl complex from the characteristic resonances exhibited in the ^{1}H NMR spectrum: a doublet of triplets is observed for the vinylic α-proton to low field at δ 9.08 [$J(H_\alpha H_\beta)$ = 17.2, $J(H_\alpha P)$ = 2.6 Hz] showing typical coupling to two mutually *trans* phosphines. The comparatively low field chemical shift for this resonance is consistent with the vinyl ligand being co-ordinated *trans* to a good donor ligand. The β-proton of the vinyl ligand gives rise to a doublet resonance at δ 5.87. An $(AB)_2$ system is observed for the tolyl substituent [δ 6.84, 6.97; J(AB) = 7.9 Hz] as well as a singlet resonance at δ 3.03 due to the methyl group. The presence of the BTD ligand is betrayed only by the microanalytical data since IR absorbances for it are typically weak and the ^{1}H NMR resonances are obscured by the phosphine resonances. The complex is thus as formulated and this is supported by

FAB MS data, and subsequent derived chemistry. In a similar manner, the red parent vinyl analogue $[Os(CH=CH_2)Cl(CO)(BTD)(PPh_3)_2]$ **4b** can also be prepared from **2c** and ethyne at ambient temperature and pressure. The ^1H NMR spectrum is more complex than that of **4a**, with the α-proton resonating as a low field multiplet at δ 8.57. The β- and β′-protons are observed at δ 4.88 [d, $J(H_\alpha H_\beta) = 17.6$] and 5.96 [dd, $J(H_\alpha H_{\beta'}) = 10.6$, $J(H_\beta H_{\beta'}) = 2.2$ Hz], respectively. Perhaps surprisingly, the species **4b** can also be prepared from a mixture of **1b** and BTD in solution on exposure to a stream of acetylene. This is however not the case with any of the other vinyl complexes discussed here. The purple enynyl complex $[Os\{C(C{\equiv}C\text{-}C_6H_4Me\text{-}4){=}CHC_6H_4Me\text{-}4\}Cl(CO)(BTD)(PPh_3)_2]$ **4c** is readily obtained from **2c** by the same route employing the diyne $(C{\equiv}CC_6H_4Me\text{-}4)_2$, which is itself obtained from a metal-mediated demercuriation of $[Hg(C{\equiv}CC_6H_4Me\text{-}4)_2]$.[25] Spectroscopic data are essentially similar to those of the species described above with the exceptions of (i) the vinylic proton which was found to resonate as a broad singlet at δ 6.43 in the ^1H NMR spectrum, and (ii) the weak ν(C≡C) IR absorption due to the free alkynyl group (Nujol: 2158, 2136 cm^{-1}). The stereochemistry of the equatorial plane of the complexes **4** does not follow unambiguously from spectroscopic data, however the geometry of the 16-electron complexes $[Ru(CPh{=}CHPh)Cl(CO)(PPh_3)_2]$,[3] $[Ru(C_6H_4Me\text{-}4)Cl(CO)(PPh_3)_2]$,[18] $[Ru(C_6H_4Me\text{-}2)Cl(CO)(PPh_3)_2]$[18] and $[Ru(CH{=}CHCH_2PPh_3)Br(CO)(PPh_3)_2]\text{-}PF_6$[4] approaches square-based pyramidal with the σ-organyl ligand occupying an apical site *trans* to the vacant co-ordination site. It is therefore reasonable that the labile BTD ligand co-ordinates in this site.

The complex $\mathbf{3a}^+$ itself provided a useful entry point into further osmium(II) σ-vinyl chemistry: the pale-brown vinyl salt $[Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(NCMe)_2(PPh_3)_2]ClO_4$ **5**·ClO_4 is obtained on stirring with an excess of 4-ethynyltoluene for 3 h at room temperature. Singlet resonances are visible in the ^1H NMR spectrum at δ 1.74 and 1.85 for the two chemically distinct and mutually *cis* co-ordinated acetonitrile ligands. The facile loss of the nitrile ligands is a feature of the FAB mass spectrum with isotopic envelopes being observed at $m/z = 902$ for $[M - MeCN]^+$ and 859 for $[M - 2MeCN]^+$, in addition to a molecular ion observed at $m/z = 945$. One acetonitrile ligand in the complex $\mathbf{5}^+$ is labile: thus treating **5**·ClO_4 with $[NEt_4]Cl$ provides the complex $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(NCMe)(PPh_3)_2]$ **6**. Spectroscopic data for this complex are identical to those for the complex obtained from the reaction of **4a** with acetonitrile. This is perhaps surprising since the nitrile in $\mathbf{5}^+$ which is *trans* to the vinyl ligand might have been expected to be the more labile of the two. Such a regioselective substitution is reminiscent of the carbonylation of the complex $[RuH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ which proceeds under ambient conditions to provide *cct*-$[RuH(CO)_2(NCMe)(PPh_3)_2]ClO_4$ and only under higher pressures and temperatures to *mer-trans*-$[RuH(CO)_3(PPh_3)_2]ClO_4$.[23,26]

The BTD ligand of complex **4a** is labile, as had been demonstrated for the related σ-aryl complex $[Os(C_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$:[24] addition of an excess of pivaloisocyanide ($CNCMe_3$) to **4a** leads to instant decolorisation of the purple solution and formation of the species $[Os(CH{=}CHC_6H_4Me\text{-}4)Cl(CO)(CNBu^t)(PPh_3)_2]$ **7a**. The same isomer of **7a** is obtained on treating **6** with $CNCMe_3$. Two intense absorptions are noted in the infrared spectrum (CH_2Cl_2) at 2144 and 1943 cm^{-1} attributed to ν(CN) and ν(CO), respectively. A singlet resonance observed at δ 0.97 in the ^1H NMR spectrum is assigned to the *tert*-butyl group in addition to a singlet at δ 2.25 for the tolyl methyl protons. The complex gives rise to an $(AB)_2$ system at δ 6.80, 6.92 [J(AB) = 7.9 Hz] and a lower field resonance at δ 7.89 due to the α-vinylic proton. This appears as a doublet of triplets showing coupling to the two mutually *trans* phosphines of 2.0 Hz as well as to the β-vinylic proton [$J(H_\alpha H_\beta) = 18.3$ Hz]. A fragmentation for loss of $CNBu^t$ is observed in the FAB mass spectrum at $m/z = 896$. As with **4**, the stereochemistry does not follow definitely from spectroscopic data, however the *trans* influence of the σ-organyl ligand may be expected to favour a vacant co-ordination site to this ligand prior to isocyanide co-ordination. In a similar manner, treating **4a** with carbon monoxide (1 atmosphere) leads to decolorisation and formation of the *cis*-dicarbonyl complex **7b**. In this case the stereochemistry at osmium is unambiguous, given the appearance of two ν(CO) IR absorptions [CH_2Cl_2, 2021, 1953 cm^{-1}] and a singlet $^{31}P\text{-}\{^1H\}$ NMR resonance (δ −6.45).

Treatment of complex **4a** with an ethanolic solution of $Na[S_2CNMe_2]\cdot 2H_2O$ results in a yellow solution from which the pale yellow complex $[Os(CH{=}CHC_6H_4Me\text{-}4)(S_2CNMe_2)(CO)(PPh_3)_2]$ **8** can be isolated in high yield (88%) (Scheme 3). The



Scheme 3 L = PPh_3, R = C_6H_4Me-4. *Reagents*: (i) $K[HB(pz)_3]$; (ii) [9]$aneS_3$; (iii) $[Bu^n_4N][B_3H_8]$; (iv) HC≡CR, heat; (v) $[Hg(C{\equiv}CR)_2]$; (vi) $Na[S_2CNMe_2]\cdot 2H_2O$; (vii) $CNCMe_3$.

methyl groups of the dithiocarbamate ligand give rise to two singlet resonances at δ 2.31 and 2.58, to slightly higher field than the tolyl methyl singlet at δ 2.20. The protons of the vinyl and the aromatic protons of the tolyl group also give rise to characteristic features. New bands of medium intensity and characteristic of the dithiocarbamate ligand were observed in the 'fingerprint' region of the infrared spectrum (Nujol) along with an intense ν(CO) absorption at 1887 cm^{-1}. The stereochemistry at ruthenium follows from the appearance of distinct NCH_3 environments [$\delta(^1H)$ 2.31, 2.58], a singlet $^{31}P\text{-}\{^1H\}$ NMR resonance (δ 8.2), and the virtual triplet patterns observed for the phenyl resonances in the ^{13}C NMR spectrum, characteristic of a *trans*-$Os(PPh_3)_2$ arrangement.

Although we have previously reported the synthesis of ruthenatetraboranes of the form $[RuR(B_3H_8)(CO)(PPh_3)_2]$ (R = H, halide, aryl, vinyl or enynyl),[9] the only known osmatetraborane is $[OsH(B_3H_8)(CO)(PPh_3)_2]$ obtained from the reaction of complex **1b** with $Tl[B_3H_8]$.[27] The complex $[Os(CH{=}CHC_6H_4\text{-}Me\text{-}4)(B_3H_8)(CO)(PPh_3)_2]$ **9** is however readily obtained on

treatment of **4a** with (less toxic) $[NBu^n_4][B_3H_8]$ in dichloromethane. The inequivalence of the phosphine environments is indicated by the AB system observed in the ^{31}P-$\{^1H\}$ NMR spectrum δ at 7.1, 7.9 with a coupling typical of a *trans*-OsP_2 arrangement [J(AB) = 300.2 Hz]. The inequivalence of the two phosphine environments arises from the butterfly "OsB_3" arrangement which provides *endo* and *exo* sites for the two phosphines. Broad resonances arising from the two distinct Os(μ-H)B protons of the triborate ligand are observed at δ −9.70 and −8.54 in the ^1H NMR, along with broad resonances to lower field for the terminal and B(μ-H)B protons and typical features due to the vinyl ligand. The ^{11}B NMR spectrum comprises two resonances at δ 2.6 and −37.2. The ^{11}B NMR spectrum of $[OsH(B_3H_8)(CO)(PPh_3)_2]$ comprises three resonances at δ 1.0, −39.5 and −40.5.[27] Thus, in the case of **9**, resonances for the two chemically inequivalent osmium bound boron nuclei are not resolved. Given that the ^{31}P-$\{^1H\}$ NMR spectrum is a sharply defined AB system, it may be assumed that this coincidence of resonances is due to an insensitivity of chemical shift towards the *trans* influences of the carbonyl and vinyl ligands rather than a fluxional process involving rotation of the ligand, which would chemically equilibrate the two phosphine environments.

The complexes $[Ru(R)Cl(CO)(PPh_3)_2]$ (R = aryl, vinyl or enynyl) react with $K[HB(pz)_3]$ (pz = pyrazol-1-yl) to provide the chiral monophosphine derivatives $[RuR(CO)(PPh_3)\{HB(pz)_3\}]$.[8] More recently we have isolated the complexes $[RuH(CA)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ (A = O or S) as intermediates in the formation of $[RuH(CA)(PPh_3)\{HB(pz)_3\}]$ from $[RuH(Cl)(CA)(PPh_3)_3]$ and $K[HB(pz)_3]$,[28] building on similar observations by Esteruelas for related reactions of $[MH(Cl)(CO)(PPr^i_3)_2]$ (M = Ru or Os).[29] In the reactions of the σ-organyl complexes of ruthenium no such intermediate was observed, however the complex $[Os(C_6H_5)(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ **10a** could be isolated from the reaction of $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ and $K[HB(pz)_3]$, and subsequently converted thermally (toluene reflux) into $[Os(C_6H_5)(CO)(PPh_3)\{HB(pz)_3\}]$ **11a**.[28] By analogy, the reaction of $K[HB(pz)_3]$ with **4a** in dichloromethane at room temperature provides the complex $[Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)_2\{\eta^2\text{-}HB(pz)_3\}]$ **10b**. This formulation was assigned principally on the basis of the AB system observed in the ^{31}P-$\{^1H\}$ NMR spectrum at δ −1.8 and 0.8 [J(AB) = 348.8 Hz] which clearly indicated non-equivalence of phosphine environments. This may be compared with the values reported for **10a** [δ 2.34, −2.62, ^2J(AB) = 301.8 Hz].[28] In the ^1H NMR spectrum seven resonances are observed in characteristic chemical shift positions for the pyrazolyl protons showing typical ^3J(HH) couplings of approximately 2 Hz. The remaining two resonances are presumed to be obscured by phosphine activity. The FAB mass spectrum exhibited no molecular ion, but instead a fragmentation for $[M - CO]^+$ at m/z = 1048. Tridentate co-ordination of the 'scorpionate' pyrazolylborate ligand is achieved by heating **10b** under reflux in toluene. The ν(CO) absorption (CH_2Cl_2) at 1913 cm^{-1} in the precursor is shifted marginally to 1918 cm^{-1} for the resulting monophosphine product $[Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)\{HB(pz)_3\}]$ **11b**. This species gives rise to a singlet resonance at δ 11.2 in the ^{31}P-$\{^1H\}$ NMR spectrum. The spectroscopic data associated with the vinyl ligand and its substituents remain essentially unchanged. Little change (*ca.* 0.2 ppm) is also observed in the chemical shift values for the pyrazolyl protons despite the transformation between bidentate and tridentate co-ordination.

The similarity between the co-ordination chemistry of the anionic 'HB(pz)$_3$' ligand and the neutral macrocycle 1,4,7-trithiacyclononane [9]aneS_3 follows from both showing a strong tendency to adopt a facial 6-electron donor co-ordination mode.[10,30,31] The organometallic chemistry of this ligand to osmium is however limited to the hydride complex $[OsH(CO)(PPh_3)([9]aneS_3)]PF_6$ and the arene complex $[Os(\eta\text{-}MeC_6H_4Pr^i\text{-}4)([9]aneS_3)][BPh_4]_2$.[32] A reaction between **4a** and [9]aneS_3 was found to proceed readily at room temperature to provide within 2 h the complex $[Os(CH{=}CHC_6H_4Me\text{-}4)(CO)(PPh_3)([9]aneS_3)]^+$ **12a**$^+$, which may be isolated as the hexafluorophosphate salt **12a**·PF_6 in 66% yield. It is noteworthy that despite these mild conditions no intermediate complex was observed involving reduced denticity of the [9]aneS_3 macrocycle in contrast to the isolation of **10b** above. The ^{31}P-$\{^1H\}$ NMR spectrum comprises a single resonance at δ 6.0 confirming that the macrocycle is co-ordinated in a tridentate manner; bidentate co-ordination would impose distinct chemical environments on the two phosphines (see above). The thiacycle gives rise to multiplet resonances between δ 1.73 and 3.06 in the ^1H NMR spectrum, due to the chirality at osmium rendering each of the twelve proton environments chemically distinct. The continuing presence of the vinyl ligand is confirmed by the resonances at δ 7.68 [dd, H_α, $J(H_\alpha H_\beta)$ = 17.1, $J(H_\alpha P)$ = 5.1 Hz] and 6.64 (d, H_β). Fragmentation of the [9]aneS_3 ligand is observed under FAB MS conditions involving loss of units of ethene at m/z = 721 for $[M - 2C_2H_4]^+$ in addition to a molecular ion apparent at m/z = 779. In a similar manner the phenyl complex $[Os(C_6H_5)(CO)(PPh_3)([9]aneS_3)]^+$ could be isolated as the PF_6 salt **12b**·PF_6 from the reaction of $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ with [9]aneS_3 and NH_4PF_6. Spectroscopic data (Experimental section) which characterise **12b**·PF_6 are directly comparable to those for **12a**·PF_6 and call for no further comment.

Alkynyl complexes (Scheme 3)

We have previously shown that the reactions of Group 8 hydrido complexes, L_nMH, with bis(alkynyl)mercurials $[Hg(C{\equiv}CR)_2]$ can (to date) take one of three interrelated courses: (i) formation of enynyl derivatives $L_{(n-1)}MC(C{\equiv}CR){=}CHR$;[5,19] (ii) formation of alkynyl complexes $L_nMC{\equiv}CR$ [20] or (iii) catalytic formation of 1,3-diynes and reformation of the original hydride complex.[20] Amongst the hydride complexes which fall into the second category is the BSD complex **2b** and the resulting product $[Ru(C{\equiv}CR)Cl(CO)(BSD)(PPh_3)_2]$ serves as a precursor to other alkynyl complexes due to the lability of the BSD ligand. The reaction of **2c** with bis(4-ethynyltolyl)mercury(II) was therefore investigated, given that it has already been noted above that **1b** fails to provide an alkynyl complex, but is rather recovered after catalysing the formation of $(C{\equiv}CC_6H_4Me\text{-}4)_2$. Stirring a dichloromethane solution of **2c** with a slight excess (2 equivalents) of $[Hg(C{\equiv}CC_6H_4Me\text{-}4)_2]$ resulted in a change to deep red and deposition of elemental mercury. The brick-red product, which could be isolated by addition of ethanol, was found to be $[Os(C{\equiv}CC_6H_4Me\text{-}4)Cl(BTD)(CO)(PPh_3)_2]$ **13**, by analogy with the related ruthenium chemistry and in contrast to the behaviour of **1b**. This complex also results in good yield from the reaction of **2c** or **4a** with an excess of 4-ethynyltoluene in refluxing tetrahydrofuran. Two characteristic absorptions in the infrared spectrum (Nujol) at 2105 and 1920 cm^{-1} may be assigned to ν(C≡C) and ν(CO) vibrations, respectively. The ^1H NMR spectrum included resonances at δ 2.29 (CH_3) and 7.41 [C_6H_4; J(AB) = 8.2 Hz, second doublet obscured by PPh_3] due to the tolyl group. The FAB mass spectrum revealed a molecular ion at m/z = 1031 (3%), however the heaviest predominant peak was, unsurprisingly, that due to loss of the BTD ligand at m/z = 894 (57%). Once again the BTD ligand is assumed to be *trans* to the strongly *trans*-effective alkynyl ligand.

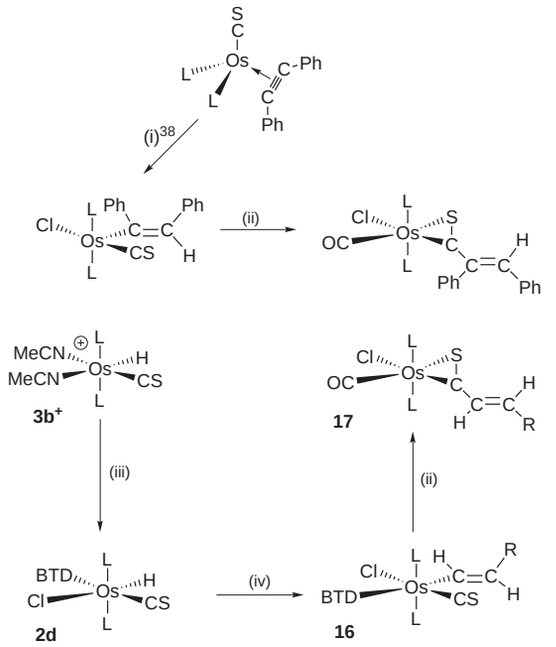
Treatment of complex **13** with $Na[S_2CNMe_2]\cdot 2H_2O$ provides the brown species $[Os(C{\equiv}CC_6H_4Me\text{-}4)(S_2CNMe_2)(CO)(PPh_3)_2]$ **14** which displays ν(C≡C) and ν(CO) absorptions in the infrared spectrum (Nujol) at 2088 and 1916 cm^{-1}, respectively, to slightly lower energy of those for the precursor **13**. The data for this complex are similar to those of the precursor with the exception of the features that arise from the dithiocarbamate ligand: as with **8**, two singlet resonances are observed in the ^1H

NMR spectrum at δ 2.24 and 2.30 corresponding to the chemically distinct methyl groups of the dithiocarbamate ligand, supporting the proposed stereochemistry. Two alternative routes to the complex **14** were also developed: the reaction between **3a**·ClO_4 and Na[S_2CNMe_2] provides high yields of the complex [OsH(S_2CNMe_2)(CO)(PPh_3)$_2$], which on heating with [Hg(C≡CC_6H_4Me-4)$_2$] in toluene produces **13**. Alternatively, the reaction of **8** with an excess of HC≡CC_6H_4Me-4 in refluxing toluene provides good yields of **14**. Recently, there have appeared a number of such alkenyl/alkynyl exchange reactions based on ruthenium and osmium,[16,33,34] although none involved dithiocarbamate complexes. The presumed mechanism of ultimate σ metathesis most likely involves oxidative addition of the terminal alkyne to provide a metal(IV) species which subsequently reductively eliminates alkene. The growing ubiquity of formally tetravalent intermediates or isolated compounds in the organometallic chemistry of ruthenium and osmium is an emergent feature of the last decade. In part this may be due to the increasing popularity of highly basic (and sterically demanding) trialkylphosphines. Such tetravalent species are also apparently mechanistically significant for PPh_3 complexes of these metals. They are however seldom observed, presumably because the less basic triarylphosphine is less effective in prolonging the lifetime of these more electronegative oxidation states. For the alkenyl/alkynyl σ-metathesis process to be facile, a vacant co-ordination site is desirable for the oxidative addition step to proceed. The strong chelation of the dithiocarbamate ligand is presumably responsible for the comparatively high temperatures required in the present process (110 °C), which probably proceeds *via* phosphine dissociation rather than chelate opening. As with the vinyl complex **8**, treatment of **13** with $CNCMe_3$ provides the orange-brown isocyanide adduct [Os(C≡CC_6H_4Me-4)Cl(CO)(CNBu^t)(PPh_3)$_2$] **15** which displays two intense absorptions at 2157 and 1961 cm^{-1} in the infrared spectrum (CH_2Cl_2) for the ν(CN) and ν(CO) absorptions, respectively. The comparatively weak ν(C≡C) is not however unambiguously identifiable. The methyl substituents of the isocyanide ligand give rise to a singlet resonance (δ 0.84) in the ^{1}H NMR spectrum to higher field than the methyl resonance of the acetylide ligand at δ 2.23.

Thiocarbonyl complexes (Scheme 4)

In our studies of carbonyl vinyl complexes of ruthenium we have found it useful also to study, in parallel, the chemistry of the thiocarbonyl analogues, where possible. This is due to the clearly enhanced propensity of thiocarbonyl ligands to enter into migratory insertion processes.[10,35–41] Two recent observations serve to highlight this process. (i) Whilst [Ru(CH=CHC_6H_4Me-4)Cl(CO)(PPh_3)$_2$] reacts with [9]aneS$_3$ and [NH_4]-PF_6 to provide the vinyl salt [Ru(CH=CHC_6H_4Me-4)(CO)-(PPh_3)([9]aneS$_3$)]PF_6, the thiocarbonyl analogue provides a thiocinnamoyl complex [Ru(η^2-SCCH=CHC_6H_4Me-4)(PPh_3)([9]-aneS$_3$)]PF_6;[10] (ii) Roper and co-workers[37] have shown that the ruthenium silyl complexes [Ru(SiR_3)Cl(CA)(PPh_3)$_2$] (A = O or S) react rapidly with CO to provide, respectively, [Ru(SiR_3)Cl-(CO)$_2$(PPh_3)$_2$] and the novel silathioacyl complex [Ru(η^2-SCSiR_3)Cl(CO)(PPh_3)$_2$], thereby showing that these ideas are not limited to carbon-based migrating ligands.

The possibility of applying the principles above to osmium thiocarbonyl chemistry was also therefore briefly investigated: the complex [OsH(Cl)(CS)(PPh_3)$_3$] **1c**[42] was treated in a completely analogous manner to **1b** to provide the salt [OsH(CS)-(NCMe)$_2$(PPh_3)$_2$]ClO_4 **3b**·ClO_4 which reacts with [NEt_4]Cl and BTD to provide [OsH(Cl)(CS)(BTD)(PPh_3)$_2$] **2d** in 99% yield. This species reacted immediately with 4-ethynyltoluene to provide [Os(CH=CHC_6H_4Me-4)Cl(CS)(BTD)(PPh_3)$_2$] **16**. Spectroscopic data for **16** are immediately comparable to those for **4a** with the exception of the characteristically intense ν(CS)



Scheme 4 L = PPh_3, R = C_6H_4Me-4. *Reagents*: (i) HCl; (ii) CO;[38] (iii) [Et_4N]Cl, BTD; (iv) HC≡CR.

absorption which appears at 1272 cm^{-1} in the infrared spectrum. The one previous example of an osmium vinylthiocarbonyl complex [Os(CPh=CHPh)Cl(CS)(PPh_3)$_2$] results from the reaction of the tolane complex [Os(PhC≡CPh)(CS)(PPh_3)$_2$] with hydrogen chloride.[38] This complex is so far unique because the synthetic route to [Os(PhC≡CPh)(CS)(PPh_3)$_2$] from [Os(CO)(CS)(PPh_3)$_3$] and PhC≡CPh is not yet generally applicable to other alkynes, *e.g.* reaction of [Os(CO)(CS)(PPh_3)$_3$] with ethyne provides instead the osmaarene [Os(SCCHCHCHCH)-(CO)(PPh_3)$_2$].[39] The complex [Os(CPh=CHPh)Cl(CS)(PPh_3)$_2$] reacts with carbon monoxide to provide the thiostilbenoyl complex [Os(η^2-SCCPh=CHPh)Cl(CO)(PPh_3)$_2$] in an analogous manner to the carbonylation of [Os(C$_6$H$_4$Me-4)Cl(CS)-(PPh_3)$_2$].[40] The vinyl complex [Os(CH=CHC_6H_4Me-4)Cl(CS)-(BTD)(PPh_3)$_2$] **16** may be assumed to be in equilibrium with the co-ordinatively unsaturated complex [Os(CH=CHC_6H_4Me-4)-Cl(CS)(PPh_3)$_2$] and accordingly this was treated with a stream of carbon monoxide. The resulting product proved to be the thiocinnamoyl complex [Os(η^2-SCCH=CHC_6H_4Me-4)Cl(CO)-(PPh_3)$_2$] **17**, in contrast to the formation of **7b** upon carbonylation of **4b**. No intermediate was isolated from this reaction. The infrared spectrum of **17** (Nujol), whilst devoid of the characteristic absorption for a terminal thiocarbonyl ligand, contained a series of bands at 1589, 1562, 1326, 1307, 1287, 1241, 970 and 919 cm^{-1} which are typical of such a metallathiirene motif.[10,38–41,43,44]

Conclusion

The results described above taken together illustrate that there is indeed a potentially rich alkyne-derived organometallic chemistry for the "OsH(Cl)(CO)(PPh_3)$_2$" fragment. The obstacle to such chemistry appears to be the unsuitability of complex **1b** as a reagent due to the lesser tendency of PPh_3 to dissociate under mild conditions. This problem has been overcome by conversion into the more labile complex [OsH(Cl)(CO)(BTD)(PPh_3)$_2$] **2c**, which appears to provide synthetically useful amounts of the desired 16-electron species "OsH(Cl)(CO)(PPh_3)$_2$" in solution. This breakthrough has provided access to new alkenyl, alkenynyl, alkynyl and thioacyl complexes of divalent osmium, which in contrast to the rapidly developing chemistry of [OsH-(Cl)(CO)(PPr^i_3)$_2$] involves air-stable compounds throughout. Furthermore, entry points into the organometallic chemistry of

osmium complexes of [9]aneS$_3$, HB(pz)$_3$ and triborate ligands have been demonstrated. The utility of [OsH(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ **3a**·ClO$_4$ and [OsH(Cl)(CS)(BTD)(PPh$_3$)$_2$] **2d** as alternative synthons for alkyne hydroosmation has also been briefly shown to offer promise.

Experimental

General comments

All experiments were routinely carried out under aerobic conditions unless otherwise stated. Solvents were used as received from commercial sources. The complexes [OsH(Cl)(CO)(PPh$_3$)$_3$],[2] [OsH(Cl)(CS)(PPh$_3$)$_3$][42] and [OsH(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$[23] and the reagents [NBu$_4$][B$_3$H$_8$],[45] K[HB(pz)$_3$][46] and (C≡CC$_6$H$_4$Me-4)$_2$[20,25] have been described elsewhere. The complex [Os(C$_6$H$_5$)Cl(CO)(PPh$_3$)$_2$] was prepared according to the method described for the synthesis of [Os(C$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$].[40] Infrared, NMR and FAB MS data were obtained using a Mattson Research Series IR spectrometer, JEOL JNM-EX270, and Autospec Q instruments, respectively. Phosphine-associated infrared data are not reported. Typically, ^{1}H NMR resonances for the BTD and BSD ligands were obscured by phosphine resonances; "t^v" indicates a virtual triplet with 'apparent' coupling constants given. The ^{13}C NMR resonances were indicative of a *trans* bis(phosphine) arrangement. The FAB mass spectra were obtained from 3-nitrobenzyl matrices; assignments are denoted by the most intense peak of isotopic envelopes confirmed by simulation and for salts M$^+$ refers to the cationic complex. Microanalytical data were obtained from the Imperial College and University of North London Microanalytical services. Crystal solvates were confirmed by ^{1}H NMR integration for dichloromethane, however this was not always possible for chloroform solvates due to overlap with phosphine resonances, or adventitious CHCl$_3$ present in the deuteriated NMR solvent. Light petroleum refers to that fraction of boiling range 40–60 °C. The majority of complexes reported could be recrystallised from mixtures of dichloromethane or chloroform and ethanol.

Preparations

[OsH(Cl)(CO)(BTD)(PPh$_3$)$_2$] 2c. The complex [OsH(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ (1.00 g, 1.08 mmol) was dissolved in dichloromethane (100 cm^3) to give a colourless solution. To this was added a solution of 2,1,3-benzothiadiazole (BTD: 0.44 g, 3.24 mmol) and [NEt$_4$]Cl (0.54 g, 3.26 mmol) in ethanol (20 cm^3). The mixture was heated for 1 h under reflux and then diluted with ethanol (50 cm^3). On slow concentration under reduced pressure orange crystals formed, which were filtered off, washed with ethanol (30 cm^3) and light petroleum (30 cm^3) and dried *in vacuo*. Yield: 0.96 g (97%). IR: (CH$_2$Cl$_2$) 1982 [ν(OsH)], 1914 cm^{-1} [ν(CO)]. (Nujol) 2146, 2129, 1974 [ν(OsH)], 1905 [ν(CO)], 1720, 1529, 1311, 1276, 925, 871, 848 and 831 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ −15.00 [t, 1 H, OsH, J(HP) = 16.2], 7.09–7.66 (m, 32 H, C$_6$H$_5$ + BTD) and 7.82 [d, 2 H, BTD, J(HH) = 9.3 Hz]; ^{31}P-{^{1}H}, δ 20.7. FAB MS: *m*/*z* (%) = 780 (4, [M − BTD]$^+$), 741 (9, [M − Cl]$^+$) and 713 (3, [M − Cl − CO]$^+$) (Found: C, 56.3; H, 3.8; N, 2.9. Calc. for C$_{43}$H$_{35}$ClN$_2$OOsP$_2$S: C, 56.4; H, 3.9; N, 3.1%).

[OsH(Cl)(CS)(BTD)(PPh$_3$)$_2$] 2d. The complex [OsH(CS)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ (**3b**·ClO$_4$: 0.40 g, 0.43 mmol) was dissolved in dichloromethane (50 cm^3) to give a colourless solution. 2,1,3-Benzothiadiazole (0.17 g, 1.25 mmol) and [NEt$_4$]Cl (0.21 g, 1.27 mmol) were added as an ethanolic solution (20 cm^3). The mixture was heated for 1 h under reflux. Further ethanol (30 cm^3) was added and yellow crystals formed on rotary evaporation. These were filtered off, washed with ethanol (30 cm^3) and light petroleum (30 cm^3) and dried *in vacuo*. Yield: 0.35 g (99%). IR: (CH$_2$Cl$_2$) 2121 [ν(OsH)] cm^{-1}; (Nujol) 2134 [ν(OsH)], 1290 [ν(CS)], 1267, 1184, 925, 890, 865 and 838 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ −11.35 [t, 1 H, OsH, J(HP) = 16.2], 7.11–7.70 (m, 32 H, PC$_6$H$_5$ + BTD) and 7.88 [d, 2 H, BTD, J(HH) = 7.9 Hz]; ^{31}P-{^{1}H}, δ 21.1. FAB MS: *m*/*z* (%) 932 (3, [M]$^+$), 967 (4, [M − Cl]$^+$), 796 (52, [M − BTD]$^+$) and 759 (15, [M − Cl − BTD]$^+$) (Found: C, 55.4; H, 3.9; N, 2.9%. Calc. for C$_{43}$H$_{35}$ClN$_2$OsP$_2$S$_2$: C, 55.5; H, 3.8; N, 3.0%).

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] 4a. The complex [OsH(Cl)(CO)(BTD)(PPh$_3$)$_2$] **2c** (0.57 g, 0.62 mmol) was dissolved in dichloromethane (20 cm^3) and 4-ethynyltoluene (0.16 cm^3, 0.15 g, 1.26 mmol) added resulting in a purple solution. This was stirred for 10 min and then diluted with ethanol (25 cm^3). Purple crystals formed on slow reduction in solvent volume (rotary evaporation) which were filtered off, washed with ethanol (20 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.62 g (97%). IR: (CH$_2$Cl$_2$) 1913 [ν(CO)], 1606 cm^{-1}; (Nujol) 1899 [ν(CO)], 1604, 1571, 1546, 1311, 1270, 923, 906, 875, 838 and 825 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 3.03 (s, 3 H, CH$_3$), 5.87 [d, 1 H, =CH, J(H$_\alpha$H$_\beta$) = 16.5], 6.84, 6.97 [(AB)$_2$, 4 H, C$_6$H$_4$, J(AB) = 7.9], 7.03–7.44 (m, 34 H, C$_6$H$_5$ + BTD) and 9.08 [dt, 1 H, OsCH$_\alpha$, J(H$_\alpha$H$_\beta$) = 17.2, J(H$_\alpha$P) = 2.6 Hz]; ^{13}C-{^{1}H} (CDCl$_3$–CH$_2$Cl$_2$ 1:10), δ 182.2 [t, CO, J(PC) = 8.6], 154.0 (m, C$_\alpha$), 139.7, 137.9 (d × 2, BTD), 134.0 [t^v, C^{2,6} (C$_6$H$_5$), J(PC) = 4.9], 133.1 [C^4 (C$_6$H$_4$)], 132.5 [t, C$_\beta$, J(PC) = 10.2], 131.3 [t^v, C^1 (C$_6$H$_5$), J(PC) = 24.3], 129.5 [C^1 (C$_6$H$_5$)], 128.8 [s(br), C^1 (C$_6$H$_4$)], 128.5 [s, C^{2,6} (C$_6$H$_4$)], 127.3 [t^v, C^{3,5} (C$_6$H$_5$), J(PC) = 4.3 Hz], 124.1 [C^{3,5} (C$_6$H$_4$)], 122.4, 120.5 (BTD) and 20.7 (CH$_3$); ^{31}P-{^{1}H}, δ −1.0. FAB MS: *m*/*z* (%) = 896 (73, [M − BTD]$^+$), 779 (22, [M − vinyl − BTD]$^+$), 753 (5, [M − CO − vinyl]$^+$), 743 (22, [M − Cl − vinyl]$^+$), 634 (9, [M − PPh$_3$]$^+$) and 606 (23, [M − CO − PPh$_3$]$^+$) (Found: C, 55.8; H, 3.7; N, 2.4. Calc. for C$_{52}$H$_{43}$ClN$_2$OsOP$_2$S·1.5CH$_2$Cl$_2$: C, 55.4; H, 4.0; N, 2.4%).

[Os(CH=CH$_2$)Cl(CO)(BTD)(PPh$_3$)$_2$] 4b. Complex **2c** (0.18 g, 0.17 mmol) was dissolved in dichloromethane (20 cm^3) and a stream of ethyne passed through the suspension for 30 s resulting in a red solution. The flask was stoppered and the mixture stirred for 40 min under an atmosphere of ethyne. Ethanol (25 cm^3) was then added and the total solvent volume slowly reduced to provide red crystals. These were filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.14 g (87%). IR: (CH$_2$Cl$_2$) 1907 cm^{-1} [ν(CO)]; (Nujol) 1907 [ν(CO)], 1658, 1587, 1556, 1531, 1334, 1313, 1272, 1263, 925, 881, 846 and 823 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 4.88 [d, 1 H, H$_\beta$, J(H$_\alpha$H$_\beta$) = 17.6], 5.96 [dd, 1 H, H$_{\beta'}$, J(H$_\alpha$H$_{\beta'}$) = 10.6, J(H$_\beta$H$_{\beta'}$) = 2.2 Hz], 7.30, 7.04, 8.05 (m × 3, 34 H, C$_6$H$_5$ + BTD) and 8.57 (m, 1 H, H$_\alpha$); ^{31}P-{^{1}H}, δ −1.3. FAB MS: *m*/*z* (%) = 936 (4, [M]$^+$), 913 (7, [M − CO]$^+$), 905 (4, [M − Cl]$^+$), 805 (2, [M − BTD]$^+$), 779 (5, [M − vinyl − BTD]$^+$), 743 (4, [M − Cl − CO − BTD]$^+$) and 713 {**4**, [Os(PPh$_3$)$_2$]$^+$} (Found: C, 55.7; H, 4.1; N, 2.8. Calc. for C$_{45}$H$_{37}$ClN$_2$OOsP$_2$S·0.5CH$_2$Cl$_2$: C, 55.5; H, 3.9; N, 2.9%).

[Os{C(C≡CC$_6$H$_4$Me-4)=CHC$_6$H$_4$Me-4}Cl(CO)(BTD)(PPh$_3$)$_2$] 4c. Complex **2c** (0.27 g, 0.30 mmol) was suspended in tetrahydrofuran (20 cm^3) and 1,4-di(*p*-tolyl)butadiyne (0.14 g, 0.61 mmol) added. The reaction was heated under reflux for 1 h under which ethanol (20 cm^3) was added. The total solvent volume was reduced to *ca*. 15 cm^3 under reduced pressure to provide purple crystals. These were filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.30 g (87%). IR: (CH$_2$Cl$_2$) 2164, 2142 [ν(C≡C)], 1909 cm^{-1} [ν(CO)]; (Nujol) 2158, 2136 [ν(C≡C)], 1897 [ν(CO)], 1719, 1603, 1587, 1571, 1528, 1504, 1308, 1270, 1175, 924, 892, 875, 846 and 811 cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H, δ 2.25, 2.38 (s × 2, 3 H × 2, CH$_3$), 6.90 [(AB)$_2$, only one doublet visible, 2 H,

CC_6H_4, J(AB) = 7.9 Hz], 6.43 [s(br), 1 H, H_β], 6.96–7.88 (m, 40 H, PC_6H_5, C_6H_4 + BTD); ^{31}P-{^{1}H}, δ −0.36. FAB MS: *m/z* (%) = 1010 (13, $[M - BTD]^+$), 975 (13, $[M - Cl - BTD]^+$), 779 (5, $M - BTD - vinyl]^+$), 743 (14, $[M - Cl - BTD - vinyl]^+$) and 713 {10, $[Ru(PPh_3)_2]^+$} (Found: C, 63.8; H, 4.3; N, 2.3. Calc. for $C_{61}H_{49}ClN_2OOsP_2S$: C, 64.0; H, 4.3; N, 2.4%).

[Os(CH=CHC$_6$H$_4$Me-4)(CO)(NCMe)$_2$(PPh$_3$)$_2$]ClO$_4$ 5·ClO$_4$. The complex $[OsH(CO)(NCMe)_2(PPh_3)_2]ClO_4$ **3a**·ClO_4 (0.10 g, 0.11 mmol) was dissolved in dichloromethane (10 cm^3) and 4-ethynyltoluene (0.03 cm^3, 0.03 g, 0.26 mmol) added. The mixture was stirred for 3 h and then diluted with ethanol (20 cm^3). Brown crystals precipitated on rotary evaporation. These were filtered off, washed with cold ethanol (2 cm^3) and light petroleum (20 cm^3) and dried. Yield: 0.09 g (79%). NB: The product is slightly soluble in ethanol. IR: (CH_2Cl_2) 1945 cm^{-1} [ν(CO)]; (Nujol) 2328 [ν(NC)], 2292 [ν(NC)], 1940 [ν(CO)], 1722, 1573, 1548, 1506, 1313, 1091 (T_d-ClO_4^-), 931, 846 and 817 cm^{-1} [$\delta(C_6H_4)$]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 1.74, 1.85 (s × 2, 3 H × 2, $NCCH_3$), 2.26 (s, 3 H, CH_3), 5.53 [d, 1 H, $=CH_\beta$, $J(H_\alpha H_\beta)$ = 17.16], 6.69, 6.96 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.92], 7.41–7.57 (m, 30 H, C_6H_5) and 7.87 [dt, 1 H, $OsCH_\alpha$, $J(H_\alpha H_\beta)$ = 17.80, J(HP) = 2.64 Hz]; ^{31}P-{^{1}H}, δ 6.2. FAB MS: *m/z* (%) = 945 (15, $[M]^+$), 902 (20, $[M - MeCN]^+$), 859 (42, $[M - 2MeCN]^+$), 831 (32, $[M - 2MeCN - CO]^+$), 779 (40, $[M - vinyl - MeCN]^+$), 743 (100, $[M - vinyl - 2MeCN]^+$) and 713 {53, $[Os(PPh_3)_2]^+$}.

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(NCMe)(PPh$_3$)$_2$] 6. (a) The complex $[Os(CH=CHC_6H_4Me\text{-}4)(CO)(NCMe)_2(PPh_3)_2]ClO_4$ **5**·ClO_4 (0.10 g, 0.10 mmol) was dissolved in dichloromethane (10 cm^3) and $[NEt_4]Cl$ (0.04 g, 0.24 mmol) added as an ethanolic solution (10 cm^3). The mixture was stirred and warmed for 20 min to give a yellow solution. All solvent was removed and the crude product extracted into dichloromethane (10 cm^3) and the extracts filtered. On evaporation of all solvent from the filtrate and trituration in diethyl ether (25 cm^3), colourless crystals were obtained. These were filtered off, washed with diethyl ether (10 cm^3) and light petroleum (10 cm^3) and dried *in vacuo*. Yield: 0.06 g (58%).

(b) A sample of the complex $[Os(CH=CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ **4a** was recrystallised from a mixture of acetonitrile and hexane to which sufficient dichloromethane had been added to ensure homogeneity. Yield quantitative. IR: (CH_2Cl_2) 1920 cm^{-1} [ν(CO)]; (Nujol) 2022 [ν(NC)], 1909 [ν(CO)], 1720, 1604, 1671, 1544, 1311, 890, 846 and 790 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 1.57 (s, 3 H, $NCCH_3$), 2.24 (s, 3 H, CH_3), 5.72 [d, 1 H, $=CH_\beta$, $J(H_\alpha H_\beta)$ = 17.16], 6.79, 6.92 [$(AB)_2$, 4 H, CC_6H_4, J(AB) = 8.26], 7.27, 7.66 (m × 2, 30 H, PC_6H_5) and 8.65 [dt, 1 H, $OsCH_\alpha$, $J(H_\alpha H_\beta)$ = 17.16, $J(H_\alpha P)$ = 2.31 Hz]; ^{31}P-{^{1}H}, δ −1.1. FAB MS: *m/z* (%) = 896 (100, $[M - MeCN]^+$), 859 (14, $[M - vinyl - MeCN]^+$), 779 (22, $[M - vinyl - MeCN]^+$), 743 (40, $[M - vinyl - Cl - MeCN]^+$), 713 {11, $[Os(PPh_3)_2]^+$} and 606 (25, $[M - MeCN - CO - PPh_3]^+$) (Found: C, 63.5; H, 5.7; N, 1.1. Calc. for $C_{51}H_{48}ClNOsOP_2S$·C_6H_{12}: C, 63.4; H, 5.7; N, 1.4%).

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)(CNBu^t)(PPh$_3$)$_2$] 7a. (a) The complex $[Os(CH=CHC_6H_4Me\text{-}4)Cl(CO)(BTD)(PPh_3)_2]$ **4a** (0.08 g, 0.08 mmol) was dissolved in dichloromethane (10 cm^3) and *tert*-butyl isocyanide (0.01 cm^3, 0.01 g, 0.09 mmol) added. The reaction was stirred for 20 min to give a colourless solution. Ethanol (20 cm^3) was added and cream crystals precipitated on rotary evaporation. These were filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried. Yield: 0.06 g (77%).

(b) Complex **5**·ClO_4 (0.05 g, 0.05 mmol) was dissolved in dichloromethane (10 cm^3) and an ethanolic (15 cm^3) solution of $[NEt_4]Cl$ (0.02 g, 0.12 mmol) added. The mixture was stirred and heated gently for 20 min and then $CNCMe_3$ (0.01 cm^3, 0.01 g, 0.09 mmol) added. After stirring for 10 min the solvent volume was reduced to give a cream precipitate. This was filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried. Yield: 0.03 g (64%). IR: (CH_2Cl_2) 2144 [ν(CN)], 1943 cm^{-1} [ν(CO)]; (Nujol) 2142 [ν(CN)], 1943 [ν(CO)], 1889, 1571, 1542, 1307, 971, 937, 890 and 840 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.97 (s, 9 H, $NCCH_3$), 2.25 (s, 3 H, CCH_3), 5.88 [d, 1 H, =CH, J(HH) = 18.05], 6.80, 6.92 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.92], 7.10–7.39 (m, 34 H, C_6H_5 + BTD) and 7.89 [dt, 1 H, OsCH, J(HH) = 18.29, J(HP) = 1.97 Hz]; ^{31}P-{^{1}H}, δ −5.0. FAB MS (R = Bu^t): *m/z* (%) = 979 (13, $[M]^+$), 896 (15, $[M - CNR]^+$), 862 (44, $[M - vinyl]^+$), 826 (7, $[M - Cl - vinyl]^+$) and 779 (3, $[M - vinyl - CNR]^+$) (Found: C, 60.6; H, 4.8; N, 1.4. Calc. for $C_{51}H_{48}ClNOsOP_2S$·$0.5CH_2Cl_2$: C, 60.6; H, 4.8; N, 1.4%).

[Os(CH=CHC$_6$H$_4$Me-4)Cl(CO)$_2$(PPh$_3$)$_2$] 7b. Complex **4a** (0.08 g, 0.08 mmol) was dissolved in dichloromethane (10 cm^3) and a stream of carbon monoxide passed through the suspension for 30 s immediately to give a pale yellow solution. The flask was stoppered and stirred for 10 min under an atmosphere of carbon monoxide. Ethanol (25 cm^3) was added and on rotary evaporation pink crystals formed which were filtered off, washed with ethanol (20 cm^3), hexane (20 cm^3) and dried *in vacuo*. Yield: 0.06 g (84%). IR: (CH_2Cl_2) 2021, 1953 cm^{-1} [ν(CO)]; (Nujol) 2011, 1947 (1935sh) [ν(CO)], 1716, 1313, 1278, 977 and 848 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.27 (s, 3 H, CH_3), 5.91 [dt, 1 H, $=CH_\beta$, $J(H_\alpha H_\beta)$ = 18.31, J(HP) = 2.24], 6.74, 6.95 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.94], 7.33, 7.62 (m × 2, 30 H, C_6H_5) and 7.47 [dt, 1 H, $OsCH_\alpha$ J(HH) = 18.55, J(HP) = 6.18 Hz]; ^{31}P-{^{1}H}, δ 6.45. FAB MS: *m/z* (%) = 924 (4, $[M]^+$), 896 (100, $[M - CO]^+$), 807 (15, $[M - vinyl]^+$), 779 (18, $[M - vinyl - CO]^+$), 771 (20, $[M - Cl - vinyl]^+$), 741 (10, $[M - Cl - CO - vinyl]^+$), 606 (30, $[M - 2CO - PPh_3]^+$), 451 (15, $[OsPPh_3]^+$) and 263 (48, $[HPPh_3]^+$) (Found: C, 61.0; H, 4.4. Calc. for $C_{47}H_{39}ClO_2OsP_2$: C, 61.1; H, 4.3%).

[Os(CH=CHC$_6$H$_4$Me-4)(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$] 8. Complex **4a** (0.07 g, 0.07 mmol) was dissolved in dichloromethane (20 cm^3) and a solution of $Na[S_2CNMe_2]$ (0.02 g, 0.14 mmol) in ethanol (5 cm^3) added. The mixture was stirred for 30 min and then diluted with ethanol (20 cm^3). Yellow crystals precipitated on rotary evaporation which were filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.06 g (88%). IR: (CH_2Cl_2) 1893 cm^{-1} [ν(CO)]; (Nujol) 1887 [ν(CO)], 1718, 1585, 1569, 1521, 1504, 1307, 1255, 1153, 970, 848 and 831 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.20 (s, 3 H, CH_3), 2.31, 2.58 (s × 2, 3 H × 2, NCH_3), 5.52 [d, 1 H, =CH, J(HH) = 17.16], 6.40, 6.80 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.92], 7.25–7.61 (m, 30 H, PC_6H_5), 8.36 [dt, 1 H, $OsCH_\alpha$, $J(H_\alpha H_\beta)$ = 17.16, $J(H_\alpha P)$ = 2.65 Hz]; ^{13}C-{^{1}H} ($CDCl_3$–CH_2Cl_2 1:10), δ 208.0 (S_2C), 186.1 [t, CO, J(PC) = 11.3], 140.8 [s(br), C_α], 134.8 [t^v, $C^{2,6}$ (C_6H_5), J(PC) = 4.9], 133.1 [t^v, C^1 (C_6H_5), J(PC) = 24.3], 132.8 [t, C_β, J(PC) = 9.7], 132.3 [C^4 (C_6H_4)], 132.0 [s(br), C^1 (C_6H_4)], 129.2 [C^4 (C_6H_5)], 128.2 [$C^{3,5}$ (C_6H_4)], 127.2 [t^v, $C^{3,5}$ (C_6H_5), J(PC) = 4.9 Hz], 123.9 [$C^{2,6}$ (C_6H_4)], 37.8, 37.0 (NCH_3) and 20.6 (CH_3); ^{31}P-{^{1}H}, δ 8.2. FAB MS: *m/z* (%) = 995 (2, $[M + H_2O]^+$), 982 (3, $[M]^+$), 878 (3, $[M + H_2O - vinyl]^+$) and 407 (56, $[M - vinyl]^+$) (Found: C, 56.1; H, 4.3; N, 1.4. Calc. for $C_{47}H_{45}NOOsP_2S_2$·$0.5CHCl_3$: C, 56.2; H, 4.5; N, 1.4%).

[Os(CH=CHC$_6$H$_4$Me-4)(B$_3$H$_8$)(CO)(PPh$_3$)$_2$] 9. Complex **4a** (0.30 g, 0.29 mmol) and $[NBu^n_4][B_3H_8]$ (0.09 g, 0.32 mmol) were dissolved in a mixture of dichloromethane (20 cm^3) and methanol (10 cm^3) and stirred for 4 h. All volatiles were removed under reduced pressure. The crude product was extracted into dichloromethane and passed through diatomaceous earth. The solvent was removed from the filtrate and the residue crystallised by ultrasonic trituration with diethyl ether (25 cm^3) to

provide a red-brown microcrystalline solid. This was filtered off, washed with diethyl ether (20 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.15 g (57%). IR: (CH_2Cl_2) 2528, 2462 [ν(BH)], 1957 cm^{-1} [ν(CO)]; (Nujol) 2524, 2460, 2148 [ν(BH)], 2107, 2017 [ν(BHOs)], 1951 [ν(CO)], 1585, 1573, 1548, 1506, 1309, 921, 848 and 782 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ −9.70, −8.54 [s(br) × 2, 1 H × 2, μ(OsHB)], −0.57, −0.41, 1.60, 2.30, 3.32, 4.05 [s(vbr) × 6, 6 H, B–H and μ-B_2H], 2.23 (s, 3 H, CH_3), 6.09 [dt, 1 H, =CH, J(HH) = 17.80, J(HP) unresolved], 6.36, 6.87 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.92 Hz] and 7.11–7.61 (m, 30 H, C_6H_5); ^{31}P-{^{1}H}, δ 7.1, 7.9 [AB, J(AB) = 300 Hz]; ^{11}B, δ 2.6 (1 B) and −37.2 (2 B, OsB). FAB MS: *m/z* (%) = 902 (25, $[M]^+$), 860 (6, $[M - B_3H_8]^+$), 744 (80, $[M - \text{vinyl} - B_3H_8]^+$), 713 {11, $[Ru(PPh_3)_2]^+$} and 635 (13, $[M - PPh_3]^+$) (Found: C, 59.5; H, 4.8. Calc. for $C_{46}H_{47}B_3OOsP_2{\cdot}0.5CH_2Cl_2$: C, 59.2; H, 5.1%).

[Os(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] 10b. Complex **4a** (0.30 g, 0.29 mmol) and K[HB(pz)$_3$] (0.11 g, 0.44 mmol) were dissolved in dichloromethane (20 cm^3) and the mixture stirred for 6 h. The purple solution was then filtered through diatomaceous earth and the filtrate diluted with ethanol (20 cm^3). A pale purple solid was obtained on reduction in solvent volume. This was filtered off, washed with cold ethanol (2 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.17 g (55%). IR: (CH_2Cl_2) 2466 [ν(BH)], 1918 cm^{-1} [ν(CO)] (Nujol) 2468 [ν(BH)], 1913 [ν(CO)], 1718, 1571, 1544, 1295, 1209, 1058, 1033, 985, 952, 919, 877 and 846 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.31 (s, 3 H, CH_3), 5.67, 5.71 [t × 2, 1 H × 2, H^4 (pz), J(HH) = 2.2], 5.89 [d, 1 H, =CH_β, $J(H_\alpha H_\beta)$ = 17.07], 6.23 [t, 1 H, H^4 (pz), J(HH) = 2.0], 6.35 [d, 1 H, H^{3,5} (pz), J(HH) = 2.2], 6.77 [$(AB)_2$, 4 H, CC_6H_4, J(AB) = 8.16, NB one doublet obscured], 6.92 [d, 1 H, H^{3,5} (pz), J(HH) = 2.2], 6.96–7.30 [m, 32 H, C_6H_5 + 2 H^{3,5} (pz)], 7.83 [d, 2 H, H^{3,5} (pz), J(HH) = 1.5] and 8.24 [dt, 1 H, OsCH_α, $J(H_\alpha H_\beta)$ = 17.32, $J(H_\alpha P)$ = 2.49 Hz]; ^{31}P-{^{1}H}, δ −1.8, 0.8 [AB, J(AB) = 348 Hz]. FAB MS: *m/z* (%) = 1048 (36, $[M - CO]^+$), 955 (5, $[M - \text{vinyl}]^+$), 778 (18, $[M - PPh_3]^+$) and 693 (8, $[M - \text{vinyl} - PPh_3]^+$) (Found: C, 61.7; H, 4.5; N, 7.7. Calc. for $C_{55}H_{49}BN_6OOsP_2$: C, 61.6; H, 4.6; N, 7.8%).

[Os(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$){HB(pz)$_3$}] 11b. (a) Complex **4a** (0.08 g, 0.08 mmol) and K[HB(pz)$_3$] (0.03 g, 0.12 mmol) were dissolved in toluene (20 cm^3) and the mixture heated under reflux for 5 min and then allowed to cool and filtered through diatomaceous earth. All solvent was removed from the filtrate under reduced pressure. Hexane (25 cm^3) was added to the residue and a cream solid obtained by ultrasonic trituration. This was filtered off, washed with hexane (20 cm^3) and dried *in vacuo*. Yield: 0.05 g (77%).

(b) The complex [Os(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)$_2${η^2-HB(pz)$_3$}] **10b** (0.05 g, 0.05 mmol) was dissolved in toluene (10 cm^3) and the reaction heated under reflux for 2 min. The resulting solution was worked up as indicated in (a) above. Yield: 0.03 g (76%). The product can be recrystallised from benzene–hexane mixtures. IR: (CH_2Cl_2) 2485 [ν(BH)], 1918 cm^{-1} [ν(CO)]; (Nujol) 2424, 2399 [ν(BH)], 1920 [ν(CO)], 1641, 1290, 1214, 1112, 1047, 966, 919, 883 and 848 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.31 (s, 3 H, CH_3), 4.6 [s(br), 1 H, BH], 5.89, 5.93 [t × 2, 1 H × 2, H^4 (pz), J(HH) = 2.2], 6.07 [t, 1 H, H^4 (pz), J(HH) = 2.2], 6.27 [d, 1 H, =CH_β, $J(H_\alpha H_\beta)$ = 17.07], 6.82 [apparent "t" (2 × d), 2 H, H^{3,5} (pz), J(HH) = 1.9], 7.01–7.35 [m, 20 H, PC_6H_5, C_6H_4 + H^{3,5} (pz)], 7.68 [apparent "t" (2 × d), 2 H, H^{3,5} (pz), J(HH) = 2.3], 7.78 [d, 1 H, H^{3,5} (pz), J(HH) = 2.0] and 8.54 [dd, 1 H, OsCH_α, $J(H_\alpha H_\beta)$ = 17.07, $J(H_\alpha P)$ = 1.48 Hz]; ^{31}P-{^{1}H}, δ 11.2. FAB MS: *m/z* (%) = 812 (100, $[M]^+$), 743 (9, $[M - pz]^+$), 695 (14, $[M - \text{vinyl}]^+$), 666 (15, $[M - \text{vinyl} - CO]^+$), 627 (8, $[M - pz - \text{vinyl}]^+$) and 597 {7, $[M - HB(pz)_3]^+$} (Found: C, 59.4; H, 4.7; N, 9.4. Calc. for $C_{37}H_{34}BN_6OOsP{\cdot}1.5C_6H_6$: C, 59.6; H, 4.7; N, 9.1%).

[Os(CH=CHC$_6$H$_4$Me-4)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ 12a·PF$_6$. Complex **4a** (0.10 g, 0.10 mmol), 1,4,7-trithiacyclononane (0.03 g, 0.17 mmol) and $[NH_4]PF_6$ (0.03 g) were dissolved in a mixture of dichloromethane (20 cm^3) and ethanol (10 cm^3). The mixture was heated under reflux for 2 h and then all solvent evaporated. The crude product was extracted into dichloromethane (2 × 10 cm^3) and the combined extracts were filtered through diatomaceous earth and then freed of volatiles under reduced pressure. Diethyl ether (25 cm^3) was added and an ochre solid obtained by ultrasonic trituration. This was filtered off, washed with diethyl ether (20 cm^3), light petroleum (20 cm^3) and dried. Yield: 0.07 g (66%). IR: (CH_2Cl_2) 1964 cm^{-1} [ν(CO)]; (Nujol) 1955 [ν(CO)], 1716, 1606, 1575, 1548, 1160 and 833 cm^{-1} [ν(PF)]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 1.83, 2.14, 2.39, 2.64, 2.78, 3.00 (m × 6, 12 H, SCH_2), 2.26 (s, 3 H, CH_3), 6.64 [d, 1 H, =CH_β, $J(H_\alpha H_\beta)$ = 17.07], 6.79, 6.98 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 8.04], 7.30–7.50 (m, 15 H, C_6H_5) and 7.68 [dd, 1 H, OsCH_α, $J(H_\alpha H_\beta)$ = 17.07, J(HP) = 5.07 Hz]; ^{31}P-{^{1}H}, δ 6.0. FAB MS: *m/z* (%) = 779 (100, $[M]^+$), 751 (4, $[M - CO]^+$), 721 (4, $[M - 2C_2H_4]^+$) and 634 (7, $[M - CO - \text{vinyl}]^+$). For microanalytical purposes the tetraphenylborate salt **12a**·BPh_4 was prepared by employing $NaBPh_4$ in place of $[NH_4]PF_6$ (Found: C, 63.8; H, 5.3. Calc. for $C_{58}H_{56}BOOsPS_3$: C, 63.5; H, 5.1%).

[Os(C$_6$H$_5$)(CO)(PPh$_3$)([9]aneS$_3$)]PF$_6$ 12b·PF$_6$. The complex $[Os(C_6H_5)Cl(CO)(PPh_3)_2]$ (0.25 g, 0.29 mmol) was dissolved in a mixture of dichloromethane (20 cm^3) and ethanol (10 cm^3). Ammonium hexafluorophosphate (0.10 g, 0.61 mmol) and 1,4,7-trithiacyclononane (0.10 g, 0.56 mmol) were added. The mixture was heated under reflux for 10 min and then freed of volatiles. The residue was extracted with dichloromethane (2 × 10 cm^3) and the combined extracts were filtered through diatomaceous earth. The filtrate was diluted with toluene (20 cm^3) and the solvent volume slowly reduced (rotary evaporator) to provide colourless crystals. These were filtered off, washed with toluene (20 cm^3) and light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.17 g (67%). IR: (CH_2Cl_2) 1963 cm^{-1} [ν(CO)]; (Nujol) 1967 [ν(CO)], 1571, 1311, 1297, 968, 839, 904 and 838 cm^{-1} [ν(PF)]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 1.80, 2.17, 2.32, 2.45, 2.63–2.93, 3.10–3.18 (m × 6, 12 H, SCH_2), 6.73–6.82 (m, 5 H, RuC_6H_5) and 7.24–7.48 (m, 15 H, PC_6H_5); ^{31}P-{^{1}H}, δ 6.3. FAB MS: *m/z* (%) 739 (100, $[M]^+$), 709 (2, $[M - C_2H_4]^+$), 683 (2, $[M - 2C_2H_4]^+$), 449 (10, $[M - CO - PPh_3]^+$), 419 (3, $[M - 2C_2H_4 - PPh_3]^+$), 390 (3, $[M - 3C_2H_4 - PPh_3]^+$) and 365 (5, $[M - CO - 3C_2H_4 - PPh_3]^+$) (Found: C, 42.8; H, 3.9. Calc. for $C_{31}H_{32}F_6OOsP_2S_3$: C, 42.2; H, 3.7%).

[OsH(S$_2$CNMe$_2$)(CO)(PPh$_3$)$_2$]. Complex **3a**·ClO_4 (0.26 g, 0.28 mmol) was dissolved in dichloromethane (20 cm^3) and a solution of $Na[S_2CNMe_2]{\cdot}2H_2O$ (0.10 g, 0.70 mmol) in ethanol (5 cm^3) added. The mixture was heated under reflux for 10 min and then diluted with ethanol (20 cm^3). Colourless crystals precipitated on rotary evaporation which were filtered off, washed with ethanol (20 cm^3) and light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.20 g (8%). IR: (CH_2Cl_2) 2026 [ν(OsH)], 1903 cm^{-1} [ν(CO)]; (Nujol) 2043 [ν(OsH)], 1989, 1901 [ν(CO)], 1857, 1584, 1571, 1514, 1310, 1260, 1156, 932, 898 and 852 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ −12.93 [t, 1 H, OsH, J(HP) = 18.16 Hz], 2.37 (s, 6 H, NCH_3), 7.27–7.34, 7.69–7.77 (m × 2, 30 H, C_6H_5); ^{31}P-{^{1}H}, δ 18.8. FAB MS: *m/z* (%) = 880 (18, $[M + H_2O]^+$), 865 (57, $[M]^+$), 832 (4, $[M - CO]^+$) and 603 (10, $[M - PPh_3]^+$) (Found: C, 55.1; H, 4.2; N, 1.7. Calc. for $C_{40}H_{37}NOOsP_2S_2$: C, 55.6; H, 4.3; N, 1.6%).

[Os(C≡CC$_6$H$_4$Me-4)Cl(CO)(BTD)(PPh$_3$)$_2$] 13. (a) Complex **2c** (0.20 g, 0.22 mmol) was dissolved in tetrahydrofuran (20 cm^3) and $[Hg(C{\equiv}CC_6H_4Me\text{-}4)_2]$ (0.18 g, 0.42 mmol) added. The mixture was heated under reflux for 10 min and then all solvent evaporated. Dichloromethane (20 cm^3) was added, the solution filtered through diatomaceous earth and the filtrate diluted with

ethanol (20 cm^3). A brick-red solid was then obtained on rotary evaporation. This was filtered off, washed with ethanol (5 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.18 g (80%). The product appears partially soluble in ethanol.

(b) Complex **2c** (0.10 g, 0.11 mmol) or **4a** (0.12 g, 0.11 mmol) and 4-ethynyltoluene (0.30 g) were heated under reflux in tetrahydrofuran (15 cm^3) for 1 h. The red solution was diluted with ethanol (30 cm^3) and concentrated under reduced pressure to provide crystals of **13**. Yield 0.080 g (71%). IR: (CH_2Cl_2) 2109 [ν(C≡C)], 1926 cm^{-1} [ν(CO)]; (Nujol) 2105 [ν(C≡C)], 1920 [ν(CO)], 1720, 1604, 1587, 1529, 1311, 1272, 1216, 925, 877 and 811 cm^{-1} [$\delta(C_6H_4)$]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.29 (s, 3 H, CH_3), 7.41 [$(AB)_2$, 2 H, C_6H_4, J(AB) = 8.19 Hz, NB second resonance obscured] and 7.03–7.85 (m, 36 H, PC_6H_5 + C_6H_4 + BTD); ^{13}C-{^{1}H} ($CDCl_3$–CH_2Cl_2 1:10), δ 179.8 [t, CO, J(PC) = 8.6], 155.3, 153.8 (BTD), 134.1 [t^v, $C^{2,6}$ (C_6H_5), J(PC) = 4.9], 131.6 [t^v, C^1 (C_6H_5), J(PC) = 24.8], 130.6 [$C^{3,5}$ (C_6H_4)], 129.6 [C^4 (C_6H_5)], 128.7 [C^4 (C_6H_4)], 128.5 [$C^{2,6}$ (C_6H_4)], 127.4 [t^v, $C^{3,5}$ (C_6H_5), J(PC) = 4.3], 126.3 [C^1 (C_6H_4)], 122.7, 120.6 (BTD), 116.6 (s, C_β), 84.5 [t, C_α, J(PC) = 14.0 Hz] and 21.0 (s, CH_3); ^{31}P-{^{1}H}, δ 0.3. FAB MS: *m/z* (%) = 1031 (3, $[M]^+$), 894 (57, $[M - BTD]^+$), 857 (4, $[M - Cl - BTD]^+$), 827 (6, $[M - Cl - CO - BTD]^+$), 779 (18, $[M - acetylide - BTD]^+$) and 743 (14, $[M - Cl - acetylide - BTD]^+$) (Found: C, 58.7; H, 4.0; N, 1.7. Calc. for $C_{52}H_{41}ClN_2OOsP_2S\cdot0.5CH_2Cl_2$: C, 58.8; H, 4.0; N, 2.6%).

[Os(C≡CC_6H_4Me-4)(S_2CNMe_2)(CO)(PPh_3)$_2$] 14. (a) The complex [OsH(S_2CNMe_2)(CO)(PPh_3)$_2$] (0.10 g, 0.12 mmol) was dissolved in toluene (20 cm^3) and [Hg(C≡CC_6H_4Me-4)$_2$] (0.06 g, 0.14 mmol) added. The mixture was heated under reflux for 8 h and then freed of volatiles. The residue was extracted with dichloromethane (20 cm^3) and the extracts were filtered through diatomaceous earth. Ethanol (20 cm^3) was then added to the filtrate and an ochre solid obtained on rotary evaporation. This was filtered off, washed with ethanol (5 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.09 g (77%).

(b) The complex [Os(C≡CC_6H_4Me-4)Cl(CO)(BTD)(PPh_3)$_2$] **13** (0.10 g, 0.10 mmol) was dissolved in dichloromethane (10 cm^3) and Na[S_2CNMe_2] (0.03 g, 0.21 mmol) added as an ethanolic solution (10 cm^3). The reaction was stirred for 1 h and then the solvent volume reduced. The resultant ochre precipitate was filtered off, washed with ethanol (20 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.08 g (82%).

(c) Complex **4a** (0.10 g, 0.10 mmol) was dissolved in toluene (10 cm^3) and 4-ethynyltoluene (0.1 cm^3, excess) added. The reaction was heated under reflux for 5 h and then all solvent evaporated. An ochre precipitate was obtained by ultrasonic trituration in ethanol (20 cm^3). This was filtered off, washed with ethanol (20 cm^3), light petroleum (20 cm^3) and dried. Yield: 0.07 g (72%). IR: (CH_2Cl_2) 2098 [ν(C≡C)], 1918 cm^{-1} [ν(CO)]; (Nujol) 2088 [ν(C≡C)], 1916 [ν(CO)], 1718, 1307, 1263, 1216, 1151, 971, 896, 846 and 815 cm^{-1} [$\delta(C_6H_4)$]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.24 (s, 3 H, CH_3), 2.30, 2.40 (s × 2, 3 H × 2, NCH_3), 6.49, 6.83 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.92 Hz] and 7.14–7.92 (m, 30 H, C_6H_5); ^{13}C-{^{1}H} ($CDCl_3$–CH_2Cl_2 1:10), δ 209.4 (S_2C), 183.4 [t, CO, J(PC) = 9.7], 134.8 [t^v, $C^{2,6}$ (C_6H_5), J(PC) = 4.9], 133.4 [t^v, C^1 (C_6H_5), J(PC) = 24.8], 133.3 [C^4 (C_6H_4)], 130.5 [$C^{2,6}$ (C_6H_4)], 129.3 [C^4 (C_6H_5)], 128.1 [$C^{3,5}$ (C_6H_4)], 127.2 [t^v, $C^{3,5}$ (C_6H_5), J(PC) = 4.9], 126.8 [C^1 (C_6H_4)], 114.0 (≡C_β), 91.8 [t, ≡C_α, J(PC) = 12.9 Hz], 37.2, 36.7 (s × 2, NCH_3) and 20.9 (s, CH_3); ^{31}P-{^{1}H}, δ 7.2. FAB MS: *m/z* (%) = 980 (8, $[M]^+$), 864 (8, $[M - acetylide]^+$), 830 (6, $[M - CO - acetylide]^+$), 718 (19, $[M - PPh_3]^+$), 691 (12, $[M - CO - PPh_3]^+$), 600 (9, $[M - acetylide - PPh_3]^+$) and 574 (18, $[M - CO - acetylide - PPh_3]^+$) (Found: C, 59.9; H, 4.4; N, 1.3. Calc. for $C_{49}H_{43}OOsP_2S_2$: C, 60.2; H, 4.4; N, 1.4%).

[Os(C≡CC_6H_4Me-4)Cl(CO)($CNBu^t$)(PPh_3)$_2$] 15. Complex **13** (0.06 g, 0.06 mmol) was dissolved in dichloromethane (20 cm^3) and $CNCMe_3$ (0.1 cm^3, excess) added. The mixture was stirred for 3 h and all volatiles then removed. Hexane (20 cm^3) was added to the residue and an orange-brown solid obtained on ultrasonic trituration. This was filtered off, washed with hexane (20 cm^3) and dried *in vacuo*. The crude product was recrystallised from a mixture of dichloromethane and ethanol. Yield: 0.04 g (71%). IR: (CH_2Cl_2) 2157 [ν(CN)], 2105 [ν(C≡C)], 1961 cm^{-1} [ν(CO)]; (Nujol) 2148 [ν(CN)], 2102 [ν(C≡C)], 1945 [ν(CO)], 1716, 1307, 1232, 1187, 1157, 971, 937, 890, 848 and 815 cm^{-1} [$\delta(C_6H_4)$]. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 0.84 (s, 9 H, $NCCH_3$), 2.23 (s, 3 H, CCH_3), 6.67, 6.85 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.8 Hz] and 7.08–7.97 (m, 30 H, PC_6H_5); ^{31}P-{^{1}H}, δ −7.1. FAB MS: *m/z* (%) (R = CMe_3) = 1084 (20, $[M + CNR + CO]^+$), 1057 (50, $[M + CNR]^+$), 977 (62, $[M]^+$), 942 (29, $[M - Cl]^+$), 894 (11, $[M - CNR]^+$), 862 (84, $[M - Cl - acetylide]^+$), 827 (22, $[M - Cl - acetylide]^+$) and 687 (20, $[M - CO - PPh_3]^+$) (Found: C, 62.7; H, 4.8; N, 1.4. Calc. for $C_{39}H_{33}ClP_2RuS$: C, 62.4; H, 4.6; N, 1.3%).

[Os(CH=CHC_6H_4Me-4)Cl(CS)(BTD)(PPh_3)$_2$] 16. The complex [OsH(Cl)(CS)(BTD)(PPh_3)$_2$] **2d** (0.10 g, 0.11 mmol) was dissolved in dichloromethane (20 cm^3) and 4-ethynyltoluene (0.02 cm^3, 0.02 g, 0.16 mmol) added to give a purple solution. This was stirred for 20 min and diluted with ethanol (25 cm^3). Pink crystals precipitated on rotary evaporation. These were isolated, washed with ethanol (20 cm^3), light petroleum (20 cm^3) and dried *in vacuo*. Yield: 0.08 g (71%). IR (Nujol): 1897, 1571, 1546, 1527, 1286, 1272 [ν(CS)], 1220, 923, 890, 875, 844, 825 and 786 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.30 (s, 3 H, CH_3), 5.98 [d(br), 1 H, =CH_β, $J(H_\alpha H_\beta)$ = 16.4], 6.91–7.47 (m, 38 H, PC_6H_5, C_6H_4 + BTD) and 9.01 [d(br), 1 H, $OsCH_\alpha$, $J(H_\alpha H_\beta)$ = 18.1 Hz]; ^{31}P-{^{1}H}, δ −1.0. FAB MS: *m/z* (%) = 1047 (2, $[M]^+$), 1012 (9, $[M - Cl]^+$), 912 (70, $[M - BTD]^+$), 877 (12, $[M - Cl - BTD]^+$), 795 (41, $[M - vinyl]^+$), 757 (20, $[M - Cl - vinyl]^+$), 650 (12, $[M - BTD - PPh_3]^+$), 612 (12, $[M - Cl - BTD - PPh_3]^+$) and 495 {16, $[Os(CS)(PPh_3)]^+$} (Found: C, 59.5; H, 4.1; N, 2.7. Calc. for $C_{52}H_{43}ClN_2OsP_2S_2$: C, 59.5; H, 4.1; N, 2.4%).

[Os(η^2-SCCH=CHC_6H_4Me-4)Cl(CO)(PPh_3)$_2$] 17. The complex [Os(CH=CHC_6H_4Me-4)Cl(CS)(BTD)(PPh_3)$_2$] **15** (0.10 g, 0.10 mmol) was dissolved in dichloromethane (10 cm^3) and a stream of carbon monoxide passed through the suspension for 30 s. On stirring for 20 min the red solution darkened. All solvent was then removed and a dark red-brown product was obtained by ultrasonic trituration in hexane (25 cm^3). This was filtered off, washed with hexane (10 cm^3), and recrystallised from a mixture of dichloromethane and ethanol. Yield: 0.07 g (78%). IR: (CH_2Cl_2) 1899 cm^{-1} [ν(CO)]; (Nujol) 1895 [ν(CO)], 1714, 1589, 1562, 1326, 1307, 1287, 1241, 970, 919, 890 and 806 cm^{-1}. NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.26 (s, 3 H, CH_3), 6.24, 6.75 [$(AB)_2$, 4 H, C_6H_4, J(AB) = 7.94], 7.00, 7.04 [AB, 2 H, CH_α=CH_β, J(AB) = 13.19 Hz], 7.26, 7.74 (m × 2, 30 H, C_6H_5); ^{31}P-{^{1}H}, δ 6.59. FAB MS: *m/z* (%) = 940 (33, $[M]^+$), 905 (44, $[M - Cl]^+$), 779 (8, $[M - SCCH=CHC_6H_4Me]^+$), 648 (7, $[M - CO - PPh_3]^+$) and 263 (13, $[HPPh_3]^+$) (Found: C, 46.2; H, 4.5. Calc. for $C_{47}H_{39}ClOOsP_2S\cdot3CHCl_3$: C, 46.3; H, 4.3%).

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Paper 8/05303K