FULL PAPER

Dalton
www.rsc.org/dalton

# Rhodium(I) and iridium(I) complexes with bidentate N,N and P,N ligands as catalysts for the hydrothiolation of alkynes †

**Suzanne Burling,[a] Leslie D. Field,[a] Barbara A. Messerle,*[b] Khuong Q. Vuong[b] and Peter Turner[a]**

[a] *School of Chemistry, University of Sydney, NSW 2006, Australia*
[b] *School of Chemical Sciences, University of New South Wales, NSW 2052, Australia. E-mail: b.messerle@unsw.edu.au*

***Received 4th April 2003, Accepted 27th May 2003***
***First published as an Advance Article on the web 22nd September 2003***

Cationic iridium(I), rhodium(I) complexes containing bis(1-methylimidazol-2-yl)methane, bim, $[M(bim)(CO)_2]BPh_4$ (M = Ir (**1**), Rh (**2**)); bis(pyrazol-1-yl)methane, bpm, $[M(bpm)(CO)_2]BPh_4$ (M = Ir (**3**), Rh (**4**)) have been shown to be effective in catalysing the regioselective addition of thiophenol to a series of alkynes. Analogous cationic and neutral Ir(I), Rh(I) complexes with the novel mixed P,N-donor bidentate ligand 1-(2-diphenylphosphino)ethylpyrazole, PyP (**5**), $[M(PyP)(COD)]BPh_4$ (M = Ir (**6**), Rh (**7**), COD = 1,5-cyclooctadiene); $[Rh(PyP)(COD)]BF_4$ (**8**); $[Ir(PyP)(CO)_2]$-$BPh_4$ (**9**); $[Rh(PyP)(CO)_2]BF_4$ (**10**); [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)) have also been synthesised, and characterised by NMR. The solid-state structures of (**6**), (**7**), (**11**) and (**12**) have been determined by single-crystal X-ray diffraction analysis. The metal complexes (**9**)–(**12**) with the mixed P,N-donor ligand, PyP are in most cases more effective in promoting the hydrothiolation of alkynes in comparison with the analogous complexes (**1**)–(**4**) with N,N-donor ligands. The iridium complexes were significantly more effective than their rhodium analogues in promoting the hydrothioloation of alkynes. The cationic complexes (**9**) and (**10**) are more effective as catalysts for the hydrothiolation of alkynes than their neutral analogues (**11**) and (**12**).

## Introduction

Transition metal catalysed addition of X–H bonds (where X = O, N, P, Si, B) to carbon–carbon double and triple bonds are highly atom efficient reactions, which typically proceed in high yield and under mild conditions. The metal-catalysed formation of C–N bonds *via* the hydroamination of carbon–carbon double and triple bonds has been achieved using lanthanide complexes as well as a number of transition metal catalysts.[1] Organometallic complexes have been particularly successful in the synthesis of five- and six-membered oxygen-containing heterocycles starting from alken-ol, alkyn-ol, enyne, and dienyne substrates.[2] Compounds containing C–S bonds commonly exhibit biological activity,[3] and are reactive and versatile intermediates in organic chemistry.[4] A general and efficient method for catalysed hydrothiolation could significantly improve synthetic routes to compounds containing C–S bonds. The transition metal catalysed synthesis of sulfur containing compounds has, however, been limited due to the fact that sulfur containing substrates can bind strongly to transition metals and often poison the catalysts.[5,6]

The addition of thiols (X = S) to alkynes is one of the most straightforward routes to vinyl sulfides, which are important synthetic intermediates.[6] Thiols are known to add to alkynes, in the presence of a radical initiator, to afford regioselectively the anti-Markovnikov products, commonly with concurrent oligomerization of the carbon centred free radical.[7] In 1976, Newton and coworkers[8] reported the Mo catalysed addition of thiophenol to the highly activated alkyne dimethyl acetylenedicarboxylate, in relatively low yields. Rhodium and palladium complexes can effectively catalyse the addition of thiophenol to unactivated alkynes and allenes giving both the Markovnikov and the anti-Markovnikov adducts,[6,9–11] as was first reported by Ogawa and coworkers in 1992.[12] The palladium catalysed chemo- and regioselective addition of thiophenol to conjugated enynes has also been demonstrated.[13] Examples of metal catalysed hydrothiolation using alkyl thiols instead of aryl thiols as substrates have been extremely limited.[14,15]

The catalyst systems tested to date for promoting the hydrothiolation reaction have primarily included complexes with phosphine donor ligands.[6] Metal complexes with N-donor ligands are also known to act as effective catalysts for a range of organic transformations.[16] We have recently shown that cationic complexes of rhodium and iridium with bidentate N-donors ligands are effective as catalysts for the hydroamination of alkynes,[17] the hydroxylation of alkynes,[18] and hydrosilation of alcohols.[19] In using N-donor ligands for the catalysis of the hydrothiolation of alkynes, however, the potentially strongly metal binding thiol substrates could readily displace the ligands from the metal centre. Mixed donor ligands containing not only N- but also additional phosphine donors should allow displacement of the N-donor without the complete displacement of ligand, and this, in principle, would provide better stability of reaction intermediates whilst maintaining the reactivity of the catalyst. A number of metal complexes with mixed donor ligands containing phosphines as well as $sp^2$-N donors from heterocycles have been reported,[20] with the focus on ligands with phosphine-pyridine[20–23] and phosphine-oxazoline donors.[22,24] Only a limited number of complexes containing mixed phosphine-imidazolyl,[25] phosphine-imidazoline,[26] and phosphine-pyrazolyl[27] donors have been reported. Complexes of mixed donor ligands with late transition metals (*e.g.* Ru, Rh, Pd, Ir) are efficient catalysts for a number of transformations, including hydrogenation,[21a,24b,d] allylic substitution[22,24b] and transfer hydrogenation.[28]

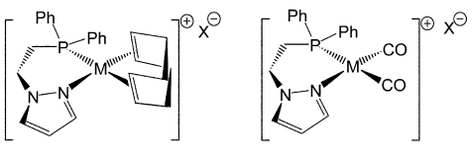
In this paper, we make a comparison between the efficiency of metal complexes with bidentate N,N-donor ligands and metal complexes with mixed P,N-donor ligands as catalysts for the hydrothiolation reaction. The synthesis of the P,N ligand 1-(2-diphenylphoshino)ethylpyrazole, PyP (**5**), is reported,[29] as well as the preparation of a series of cationic and neutral iridium(I) and rhodium(I) complexes with bidentate N,N and P,N donor ligands $[Ir(bim)(CO)_2]BPh_4$ (**1**) (bim = bis(1-methylimidazol-2-yl); $[M(PyP)(COD)]BPh_4$ (M = Ir (**6**), Rh (**7**));

† Based on the presentation given at Dalton Discussion No. 6, 9–11th September 2003, University of York, UK.

Electronic supplementary information (ESI) available: Listing of $^1$H NMR data for the alkenyl protons of alkenyl sulfides. See http://www.rsc.org/suppdata/dt/b3/b303774f/

DOI: 10.1039/b303774f

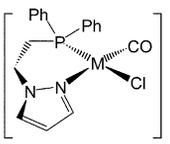
$[Rh(PyP)(COD)]BF_4$ (**8**); $[Ir(PyP)(CO)_2]BPh_4$ (**9**); $[Rh(PyP)(CO)_2]BF_4$ (**10**); and [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)). The solid-state structures of (**6**), (**7**), (**11**) and (**12**) were determined by single-crystal X-ray diffraction analysis. The efficiency of cationic iridium(I) and rhodium(I) complexes containing the N,N-donor ligands bim, and bis(pyrazol-1-yl)methane, bpm, $[M(bim)(CO)_2]BPh_4$ (M = Ir (**1**), Rh (**2**)) and $[M(bpm)(CO)_2]BPh_4$ (M = Ir (**3**), Rh (**4**)) as catalysts for the regioselective addition of thiophenol to a series of alkynes is compared to that of complexes (**9**)–(**12**) with mixed P,N donor ligands.



(**6**) M = Ir, X = $BPh_4$
(**7**) M = Rh, X = $BPh_4$
(**8**) M = Rh, X = $BF_4$



(**9**) M = Ir, X = $BPh_4$
(**10**) M = Rh, X = $BF_4$

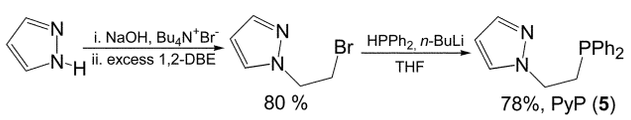


(**11**) M = Ir
(**12**) M = Rh

## Results and discussion

### Synthesis of 1-(2-diphenylphosphino)ethylpyrazole, PyP (5)

The bidentate P,N ligand PyP (**5**) was synthesised in two steps from pyrazole (Scheme 1). The synthesis of the intermediate 1-(2-bromoethyl)pyrazole was performed by modifying a literature method,[30] where the use of the phase transfer catalyst tetrabutylammonium bromide at a concentration of only 10 mol% rather than 100 mol% was found to give improved yields. Very recently, Ros and Mathieu have reported the synthesis of the similar ligand 1-(2-diphenylphosphinoethyl)-3,5-dimethylpyrazole and complexes of this ligand with Rh(I).[27b]

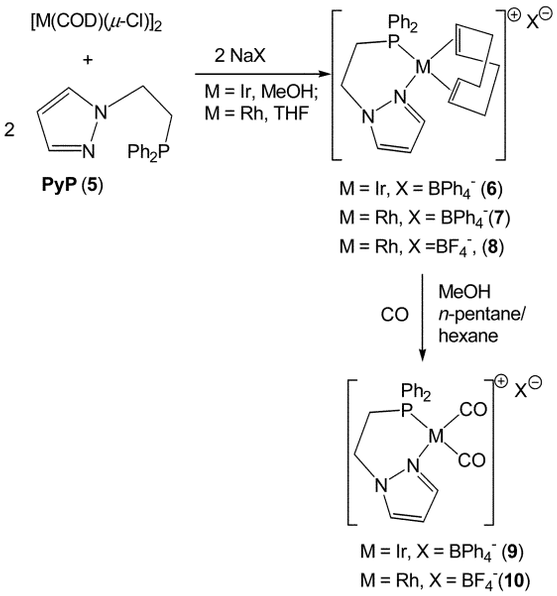



**Scheme 1**

### Synthesis of metal complexes

**(a) Synthesis of $[Ir(PyP)(COD)]BPh_4$ (6) and $[Rh(PyP)(COD)]BPh_4$ (7).** The cationic iridium complex $[Ir(PyP)(COD)]BPh_4$ (**6**) was synthesised in excellent yields (> 90%) by simply mixing the ligand PyP (**5**), $[Ir(COD)(\mu\text{-}Cl)]_2$ and $NaBPh_4$ in methanol followed by filtration to collect the resulting precipitate (Scheme 2). Complex (**6**) was isolated as an air-stable, bright orange solid.

The rhodium complex (**7**) was prepared in excellent yield by the slow addition of PyP (**5**) into a dilute solution of $[Rh(COD)(\mu\text{-}Cl)]_2$ in slight excess of a 2 : 1 molar ratio, followed by the addition of $NaBPh_4$. The complex was isolated as an air-stable, bright yellow solid. Attempts to form the rhodium complex (**7**) by reaction of the starting materials in a different sequence led to the formation of mixtures. Mixing PyP (**5**), $[Rh(COD)(\mu\text{-}Cl)]_2$ and $NaBPh_4$ in a 2 : 1 : 2 molar ratio resulted in the formation of a mixture of two metal complexes in the ratio of approximately 0.6 : 1.0 as evidenced by $^{31}P\{^1H\}$ spectroscopy. The major product gave rise to a rhodium-coupled doublet in the $^{31}P\{^1H\}$ spectrum at $\delta$ 28.2 ppm (acetone-$d_6$, $^1J$(Rh–P) = 148.6 Hz), and this was due to the $^{31}P$




**Scheme 2**

of complex (**6**). The other product gave rise to a rhodium-coupled doublet at $\delta$ 44.2 ppm (acetone-$d_6$, $^1J$(Rh–P) = 170.6 Hz) in the $^{31}P\{^1H\}$ spectrum, and this was attributed to $[Rh(PyP)_2]BPh_4$. The identity of this product was confirmed by ES-MS. The two phosphorus atoms in $[Rh(PyP)_2]BPh_4$ were assigned to be *cis* to each other, based on the observed chemical shifts and on comparison with other known Rh–P coupling constants.[23d,27b] Two-dimensional NMR spectroscopy (NOESY and $^1H$, $^{13}C$-HMQC) provided a more complete NMR characterisation of these complexes. The observation of broad proton resonances due to metal bound COD suggests these complexes undergo fluxional processes in solution at room temperature.

The solid-state structures of (**6**) and (**7**) were determined by single-crystal X-ray diffraction analyses (Table 1). Crystals suitable for X-ray crystal analysis were obtained by vapour diffusion of hexane into a solution of (**6**) in THF, and layering a dichloromethane solution of (**7**) with diethyl ether. ORTEP[31,32] depictions, including the atom numbering scheme, of the cations of (**6**) and (**7**) are shown in Fig. 1. Selected bond lengths and bond angles for the inner coordination sphere are listed in Table 2.

In the solid state the (**6**) and (**7**) complex molecules are effectively inverted with respect to each other, with both compounds having crystallised in the non-centrosymmetric space group *Fdd*2 (no. 43). The metal coordination spheres are square planar, with the iridium and rhodium atoms located only 0.039(1) and 0.035(1) Å and from the coordination planes defined by N(1), P(1), and the mid points of C(1)–C(2) and C(5)–C(6), respectively. The bite angles of 89.47(6) and 88.86(4)° for P(1)–M–N(1) (M = Ir(1), Rh(1)), are close to the ideal of 90° expected for square-planar complexes, which implies a very low level of ring strain due to the chelation of the PyP ligand. These angles are significantly larger than the angle (82.68°) reported in the X-ray structure of the analogous Rh(I) complex $[Rh(Me_2PyP)(COD)]BF_4$,[27b] which is likely to be due to the steric effect imposed by the relatively bulky $CH_3$ group interacting with the COD ligand in the $[Rh(Me_2PyP)(COD)]BF_4$ complex. Both of the six-membered metallocycles of (**6**) and (**7**) defined by M(1) (M = Ir, Rh), N(1), N(2), C(12), C(13) and P(1) have pseudo-boat conformations. Similar pseudo-boat conformations have also been observed in the reported X-ray structures of related complexes.[27b,23d,33] All the M–N, M–P and M–C bond distances (M = Ir, Rh, Table 2) of (**6**) and (**7**) are within the ranges reported for similar complexes.[23d,27b,34]

**Table 1** Crystallographic data for [Ir(PyP)(COD)]$BPh_4$ (**6**) and [Rh(PyP)(COD)][$BPh_4$ (**7**)

| | (**6**) | (**7**) |
|---|---|---|
| Empirical formula | $C_{49}H_{49}BIrN_2P$ | $C_{49}H_{49}$ $BN_2PRh$ |
| $M$/g mol$^{-1}$ | 899.88 | 810.59 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Fdd*2 (no. 43) | *Fdd*2 (no. 43) |
| $a$/Å | 34.832(8) | 34.868(8) |
| $b$/Å | 55.975(13) | 56.131(12) |
| $c$/Å | 8.1474(19) | 8.1496(18) |
| $V$/Å$^3$ | 15885(6) | 15950(6) |
| $D_c$/g cm$^{-3}$ | 1.505 | 1.356 |
| $Z$ | 16 | 16 |
| $T$/K | 150(2) | 150(2) |
| $\lambda$(Mo-K$\alpha$)/Å | 0.71073 | 0.71073 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.344 | 0.508 |
| Crystal size/mm | 0.417 × 0.251 × 0.178 | 0.290 × 0.240 × 0.210 |
| Crystal colour | Orange | Orange |
| Crystal habit | Prism | Prism |
| $T$(Gaussian)$_{min,max}$ | 0.316, 0.567 | 0.864, 0.929 |
| $2\theta_{max}$/° | 56.68° | 56.68° |
| *hkl* Range | −46 46, −74 74, −10 10 | −45 45, −74 74, −10 10 |
| $N$ | 39465 | 38657 |
| $N_{ind}$ ($R_{merge}$) | 9565 (0.0362) | 9654 (0.0359) |
| $N_{obs}$ ($I > 2\sigma(I)$) | 9216 | 9133 |
| GoF (all data) | 1.590 | 1.097 |
| $R1$ ($F$, $I > 2\sigma(I)$) | 0.0179 | 0.0240 |
| $wR2$ ($F^2$, all data) | 0.0363 | 0.0555 |

$R1 = \Sigma||F_o| - |F||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_o^2)^2/\Sigma(wF_o^2)^2)^{1/2}$ for all reflections, $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o + 2F_o^2)/3$; $X =$ 0.01, $Y = 0.0$ for (**6**), $X = 0.03$, $Y = 0.3$ for (**7**).

**Table 2** Selected bond lengths (Å) and angles (°)[a] of the inner coordination sphere of [Ir(PyP)(COD)]$BPh_4$ (**6**) and [Rh(PyP)(COD)]-$BPh_4$ (**7**)

| [Ir(PyP)(COD)]$BPh_4$ (**6**) | | [Rh(PyP)(COD)]$BPh_4$ (**7**) | |
|---|---|---|---|
| Ir(1)–P(1) | 2.2943(8) | Rh(1)–P(1) | 2.2885(6) |
| Ir(1)–N(1) | 2.086(2) | Rh(1)–N(1) | 2.1053(16) |
| Ir(1)–C(1) | 2.224(3) | Rh(1)–C(1) | 2.2476(19) |
| Ir(1)–C(2) | 2.214(2) | Rh(1)–C(2) | 2.2504(19) |
| Ir(1)–C(5) | 2.145(3) | Rh(1)–C(5) | 2.1524(18) |
| Ir(1)–C(6) | 2.126(3) | Rh(1)–C(6) | 2.139(2) |
| P(1)–Ir(1)–N(1) | 89.47(6) | P(1)–Rh(1)–N(1) | 88.86(4) |
| P(1)–Ir(1)–C(5) | 88.69(7) | P(1)–Rh(1)–C(5) | 88.58(5) |
| P(1)–Ir(1)–C(6) | 97.55(7) | P(1)–Rh(1)–C(6) | 97.57(5) |
| N(1)–Ir(1)–C(1) | 87.43(9) | N(1)–Rh(1)–C(1) | 87.85(7) |
| N(1)–Ir(1)–C(2) | 96.19(9) | N(1)–Rh(1)–C(2) | 96.86(7) |
| C(1)–Ir(1)–C(6) | 81.25(10) | C(1)–Rh(1)–C(6) | 81.69(7) |
| C(2)–Ir(1)–C(5) | 80.17(10) | C(2)–Rh(1)–C(5) | 80.38(7) |
| C(1)–Ir(1)–C(5) | 96.54(10) | C(1)–Rh(1)–C(5) | 96.57(7) |
| C(2)–Ir(1)–C(6) | 88.08(10) | C(2)–Rh(1)–C(6) | 87.94(7) |

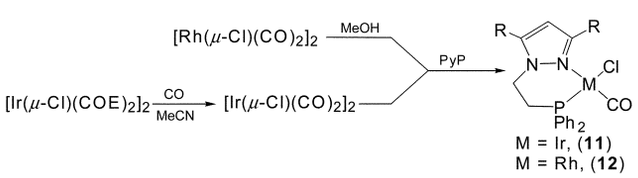
[a] Estimated standard deviations in the least significant figure are given in parentheses.

**(b) Synthesis of [Ir(PyP)$(CO)_2$]$BPh_4$ (9), [Rh(PyP)(COD)]-$BF_4$ (8) and [Rh(PyP)$(CO)_2$]$BF_4$ (10).** The iridium(I) dicarbonyl complex [Ir(PyP)$(CO)_2$]$BPh_4$ (**9**) was synthesised by the displacement of COD from the [Ir(PyP)(COD)]$BPh_4$ (**6**) under an atmosphere of carbon monoxide (Scheme 1). Complex (**9**) was isolated as a mildly air-sensitive bright yellow solid. In THF-$d_8$, (**9**) decomposed very quickly at room temperature (less than 30 min under a nitrogen atmosphere). The complex was characterised by $^1$H and $^{31}$P{$^1$H} NMR. The IR spectrum with two strong absorption bands at 2060 and 2022 cm$^{-1}$ supports the presence of two inequivalent, metal bound, carbonyl groups.

Attempts to synthesise [Rh(PyP)$(CO)_2$]$BPh_4$ from [Rh(PyP)-(COD)]$BPh_4$ (**7**) using similar methods were not successful. The IR spectrum of the solid formed immediately following the equivalent CO displacement reaction shows that carbon monoxide does displace COD, but the product is not stable. The recent report of the more stable complex [Rh($Me_2$PyP)-$(CO)_2$]$BF_4$ [27b] suggested that the tetraphenylborate anion might destabilise the complex, by for example coordination at the Rh centre.[35]

[Rh(PyP)(COD)]$BF_4$ (**8**) was prepared using same method that was used for the preparation of the analogous compound [Rh(PyP)(COD)]$BPh_4$ (**7**). [Rh(PyP)$(CO)_2$]$BF_4$ (**10**) was synthesised by placing a methanol/hexane suspension of (**7**) under an atmosphere of carbon monoxide to displace the COD coligand. [Rh(PyP)$(CO)_2$]$BF_4$ (**10**) was isolated as a pale yellow solid in high yield. The use of a mixture of non-miscible solvents is effective in separating the ionic product (in the methanol phase) and the displaced COD (in the hexane phase), preventing re-coordination of COD.

**(c) Synthesis of [Ir(PyP)(CO)Cl] (11) and [Rh(PyP)(CO)-Cl] (12).** [Rh(PyP)(CO)Cl] (**12**) was prepared by the slow addition of PyP into a methanol solution of [Rh$(CO)_2$(μ-Cl)]$_2$ (Scheme 3). The neutral complex (**12**) precipitated directly from the solution. The $^{13}$C{$^1$H} NMR shows the peak due to CO at $\delta$ 188.7 ppm as a doublet of doublets: $^1J$(Rh–C) = 71.2 Hz, $^2J$(P–C) = 18.2 Hz. The small phosphorus coupling constant indicates that the CO group is *cis* to the phosphine group. The IR spectrum of (**12**) shows a strong absorbance $\nu$CO at 1995 cm$^{-1}$, which very similar to the observed $\nu$CO = 1990 cm$^{-1}$ of [Rh(PN)(CO)Cl][23d] (PN = 1-(2-pyridyl)-2-diphenylphosphino)-ethane), where the CO was assigned as *cis* to P in the metal centre.




**Scheme 3**

The synthesis of the Ir analogue of (**12**), [Ir(PyP)(CO)Cl] (**11**), could not be achieved following a similar preparation to that of (**12**) because the isolation of [Ir$(CO)_2$(μ-Cl)]$_2$, which is equivalent to the conveniently prepared precursor [Rh$(CO)_2$-(μ-Cl)]$_2$, has not been reported. Roberto *et al.* [36] reported a

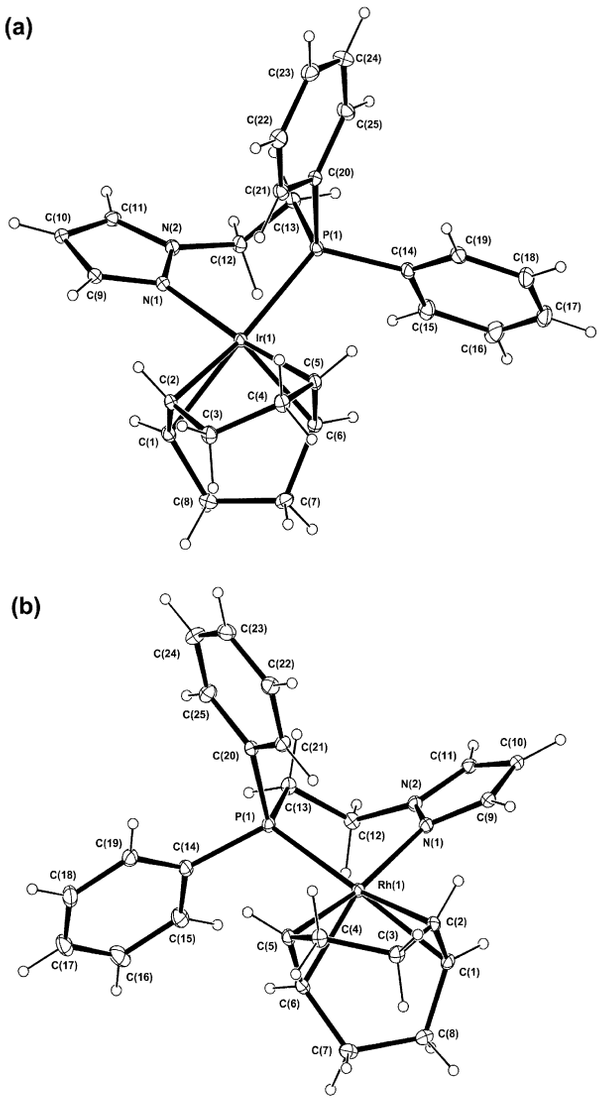



**Fig. 1** The ORTEP depictions of (a) $[Ir(PyP)(COD)]^+$ (**6**) and (b) $[Rh(PyP)(COD)]^+$ (**7**) as viewed from top of the coordination plane showing the pseudo-boat conformation of the $[MNNCH_2CH_2P]$ metallocycles at 20% thermal ellipsoids for the non-hydrogen atoms.

convenient generation of $[Ir(CO)_2(\mu\text{-}Cl)]_2$ *in situ* from the easily obtained precursor $[Ir(COE)_2(\mu\text{-}Cl)_2]_2$ (COE = *cis*-cyclooctene) in acetonitrile, and was able to use this precursor to prepare several neutral Ir(I) complexes with P or N donor ligands. Complex (**11**) was synthesised by the slow addition of PyP into freshly generated $[Ir(CO)_2(\mu\text{-}Cl)]_2$ in acetonitrile (Scheme 3). [Ir(PyP)(CO)Cl] (**11**) was collected as a yellow solid after partial removal of solvent *in vacuo*. The $^{13}C\{^1H\}$NMR ($CD_2Cl_2$) shows the CO resonance at $\delta$ 174.4 ppm as a phosphorus-coupled doublet with $^3J$(P–C) = 13.8 Hz, indicating that CO is *cis* to the phosphine group. The IR absorbance $\nu$CO = 1983 $cm^{-1}$ is in agreement with $\nu$CO = 1976 $cm^{-1}$ for [Ir(PN)(CO)Cl][23d] (PN = 1-(2-pyridyl)-2-(diphenylphosphino)ethane, CO *cis* to P) whose solid-state structure has been determined. The analogous Ir compound [Ir(PN)(CO)Cl] (PN = 1-(2-pyridyl)-2-diphenylphosphino)ethane) was prepared by the reaction of PN with $Li[Ir(CO)_2Cl_2]$.[37]

The solid-state structures of (**11**) and (**12**) were determined by single-crystal X-ray diffraction analysis (Table 3). Crystals suitable for single-crystal X-ray analysis were obtained from careful layering dichloromethane solutions of (**11**) and (**12**) with hexane. ORTEP[31] depictions, including the atom numbering scheme of (**11**) and (**12**) are shown in Fig. 2. The selected bond lengths and bond angles for the inner coordination spheres are listed in Table 4.

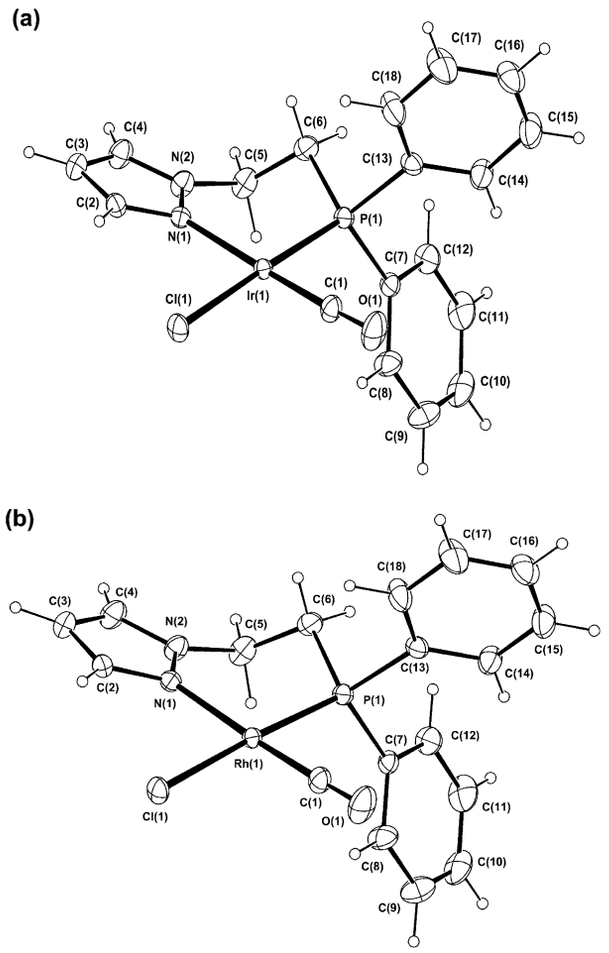



**Fig. 2** The ORTEP depictions of (a) [Ir (PyP)(CO)Cl] (**11**) and (b) [Rh(PyP)(CO)Cl] (**12**) at 20% thermal ellipsoids for the non-hydrogen atoms as viewed from tops of the coordination planes.

The solid-state structures of (**11**) and (**12**) are very similar. The coordination spheres around the metal centres are both slightly distorted square planar. The phosphorus and the chlorine atoms are *trans*, as are the nitrogen atom and the CO ligand, as observed for the solution structure using NMR. The bite angles P(1)–M(1)–N(1) (M = Ir, 93.21(5)°; M = Rh, 92.93(5)°) are slightly larger than the ideal value 90°, and are larger than the value (88.1°) reported for the analogous [Ir(PN)(CO)Cl][23d] (PN = 1-(2-pyridyl)-2-(diphenylphoshino)ethane). The *trans* L–M–L′ angles P(1)–M(1)–Cl(1) (M = Ir, 178.1°; M = Rh, 177.0°) and N(1)–M(1)–C(1) (M = Ir, 175.4°; M = Rh, 175.0°) deviate slightly from 180°. All the remaining *cis* L–M–L′ (M = Ir, Rh) angles are extremely close to the ideal orthogonal angle and fall within the range 88.3–89.8° (Table 4). All the M–P, M–N, M–Cl, M–C bond lengths (M = Ir, Rh) are all within the reported values for similar complexes.[23d,38] Both of six membered metallocycles defined by P(1)–C(6)–C(5)–N(2)–N(1)–M(1) (M = Ir, Rh) adopt the same highly distorted boat conformation.

### Metal complex catalysed hydrothiolation of alkynes with thiophenol

The reactions between thiophenol and a number of terminal alkynes (phenylacetylene, (**13a**); propargyl alcohol, (**13b**); 1-pentyne, (**13c**); and (trimethylsilyl)acetylene, (**13d**)) in the presence of catalytic quantities of complexes $[M(bim)(CO)_2]BPh_4$ (M = Ir (**1**), Rh (**2**)); $[M(bpm)(CO)_2]BPh_4$ (M = Ir (**3**), Rh (**4**)); $[M(PyP)(CO)_2]X$ (M = Ir, X = $BPh_4^-$ (**9**), M = Rh, X = $BF_4^-$ (**10**)); and [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)) were examined (Scheme 4). The reactions were performed under an

**Table 3** Crystallographic data for [Ir(PyP)(CO)Cl] (**11**) and [Rh(PyP)(CO)Cl] (**12**)

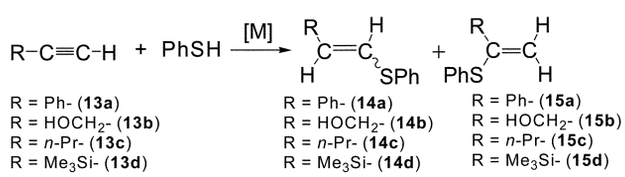
| | [Ir(PyP)(CO)Cl] (**11**) | [Rh(PyP)(CO)Cl] (**12**) |
|---|---|---|
| Empirical formula | $C_{18}H_{17}ClIrN_2OP$ | $C_{18}H_{17}ClN_2OPRh$ |
| $M$/g mol$^{-1}$ | 535.96 | 446.67 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ (no. 14) | $P2_1/c$ (no. 14) |
| $a$/Å | 11.912(3) | 11.908(3) |
| $b$/Å | 13.040(3) | 13.063(3) |
| $c$/Å | 12.137(3) | 12.087(3) |
| $\beta$/° | 97.564(4) | 97.498(4) |
| $V$/Å$^3$ | 1868.8(7) | 1864.2(8) |
| $D_c$/g cm$^{-3}$ | 1.905 | 1.591 |
| $Z$ | 4 | 4 |
| $T$/K | 295(2) | 294(2) |
| $\lambda$(Mo-K$\alpha$)/Å | 0.71073 | 0.71073 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 7.380 | 1.152 |
| Crystal size/mm | 0.408 × 0.144 × 0.058 | 0.442 × 0.045 × 0.032 |
| Crystal colour | Yellow | Yellow |
| Crystal habit | Blade | Blade |
| $T$(Gaussian)$_{min,max}$ | 0.172, 0.657 | 0.760, 0.964 |
| $2\theta_{max}$/° | 56.54 | 56.64 |
| $hkl$ Range | −15 15, −17 17, −16 16 | −15 15, −17 17, −16 16 |
| $N$ | 18392 | 18974 |
| $N_{ind}$ ($R_{merge}$) | 4469(0.0323) | 4519 (0.0432) |
| $N_{obs}$ ($I > 2\sigma(I)$) | 3924 | 3157 |
| GoF (all data) | 1.165 | 1.064 |
| $R1$ ($F$, $I > 2\sigma(I)$) | 0.0167 | 0.0263 |
| $wR2$ ($F^2$, all data) | 0.0407 | 0.0436 |

$R1 = \Sigma||F_o| - |F||/\Sigma|F_o|$ for $F_o > 2\sigma(F_o)$; $wR2 = (\Sigma w(F_o^2 - F_o^2)^2/\Sigma(wF_o^2)^2)^{1/2}$ for all reflections; $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$ where $P = (F_o + 2F_o^2)/3$; $X = 0.02$, $Y = 0.0$ for (**11**), $X = 0.01$, $Y = 0.0$ for (**12**).

**Table 4** Selected bond lengths (Å) and angles (°)[a] of the inner coordination spheres of [Ir(PyP)(CO)Cl] (**11**) and [Rh(PyP)(CO)Cl] (**12**)

| [Ir(PyP)(CO)Cl] (**11**) | | [Rh(PyP)(CO)Cl] (**12**) | |
|---|---|---|---|
| Ir(1)–P(1) | 2.2161(7) | Rh(1)–P(1) | 2.2150(7) |
| Ir(1)–N(1) | 2.119(2) | Rh(1)–N(1) | 2.1233(18) |
| Ir(1)–C(1) | 1.811(3) | Rh(1)–C(1) | 1.798(3) |
| Ir(1)–Cl(1) | 2.3890(7) | Rh(1)–Cl(1) | 2.3931(7) |
| P(1)–Ir(1)–N(1) | 93.21(5) | P(1)–Rh(1)–N(1) | 92.93(5) |
| N(1)–Ir(1)–Cl(1) | 88.28(5) | N(1)–Rh(1)–Cl(1) | 89.76(5) |
| Cl(1)–Ir(1)–C(1) | 89.72(8) | Cl(1)–Rh(1)–C(1) | 88.86(8) |
| C(1)–Ir(1)–P(1) | 88.88(8) | C(1)–Rh(1)–P(1) | 88.58(8) |
| N(1)–Ir(1)–C(1) | 175.40(10) | N(1)–Rh(1)–C(1) | 174.93(10) |
| Cl(1)–Ir(1)–P(1) | 178.14(2) | Cl(1)–Rh(1)–P(1) | 176.96(2) |

[a] Estimated standard deviations in the least significant figure are given in parentheses.




**Scheme 4**

atmosphere of nitrogen, generally on a small scale in NMR tubes. The formation of products was monitored by $^1$H NMR. The identities of products were confirmed by GC-MS. The chemical shifts of the resonances due to the alkenyl hydrogens of products **14a**–**d**,**15b** are tabulated in the supplementary material. Good to excellent yields were obtained in many cases under mild conditions using a 1 mol% catalyst loading, although the yields varied significantly over the full range of metal complexes. In most cases, only the anti-Markovnikov addition products were observed (Table 5).

This is the first report of the application of iridium complexes as catalysts for the formation of C–S bonds.[6] For the series of complexes investigated here, iridium complexes were significantly more efficient in promoting the addition of thiophenol to alkynes than their rhodium analogues. Where the rhodium complexes were effective catalysts for the addition of thiophenol to phenylacetylene, selected iridium complexes were more effective as catalysts for the full range of alkyne substrates investigated. In most cases, the iridium complexes afforded similar or better reaction yields, under milder conditions and with a lower catalyst loading, than those that have been reported using palladium and rhodium catalysts[9] for similar transformations.

On comparing the complexes with bidentate nitrogen donors (**1**)–(**4**), and the complexes with the P,N bidentate ligand (**9**)–(**12**), those complexes containing the mixed donor ligand PyP were more efficient catalysts for hydrothiolation. Reactions catalysed by complexes with PyP (**5**) proceeded faster under similar conditions. In some cases, the complexes containing the PyP ligand were able to facilitate transformations which were not promoted by complexes with N,N ligands. The two iridium complexes, $[Ir(PyP)(CO)_2]BPh_4$ (**9**), and [Ir(PyP)(CO)Cl] (**11**) and the cationic rhodium complex $[Rh(PyP)(CO)_2]BF_4$ (**10**) were able to promote the hydrothiolation of 1-pentyne with PhSH giving only the anti-Markovnikov products in excellent yields (Table 5). This transformation could not be realised using the remaining catalysts under investigation (Table 5).

Cationic complexes were more effective than their corresponding neutral complexes in catalysing hydrothiolation. Hydrothiolation reactions that were promoted by cationic complexes generally proceeded at faster rates and gave higher product yields (Table 5). One exception was the reaction between PhSH and (trimethylsilyl)acetylene, where almost all of the catalysts tested failed as effective catalysts. The exception was the neutral complex [Ir(PyP)(CO)Cl] (**11**), where the *E* isomer of the anti-Markovnikov products was produced exclusively in 45% yield after 30 h at 50 °C. The difference in the efficiency of cationic complexes in comparison to the neutral complexes was more clearly illustrated for complexes containing the mixed donor PyP (**5**) ligand.

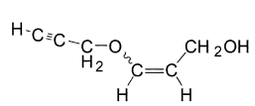
Complexes (**9**) and (**10**) were so reactive that in the reaction of PhSH with propargyl alcohol, in addition to the expected

**Table 5** Metal complex catalysed addition of thiophenol to alkynes (phenylacetylene, (**13a**); propargyl alcohol, (**13b**); 1-pentyne, (**13c**); and (trimethylsilyl)acetylene, (**13d**)). Catalytic quantities of complexes ([M(bim)$(CO)_2$]$BPh_4$ (M = Ir (**1**), Rh (**2**)); [M(bpm)$(CO)_2$]$BPh_4$ (M = Ir (**3**), Rh (**4**)); [M(PyP)$(CO)_2$]X (M = Ir, X = $BPh_4^-$ (**9**), M = Rh, X = $BF_4^-$ (**10**)); [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)) were used.[a] The maximum product yields, along with relative amounts of *E*/*Z* isomers, are given along with the time taken to reach maximum yield

| Alkyne | Catalyst | Temp./°C | Time[b]/h | Product yield (*E*/*Z*) (%)[c] | |
|---|---|---|---|---|---|
| | | | | **14a** | **15a** |
| Phenyacetylene (**13a**) | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**) | 25 | 5 | 95 (33/67) | 0 |
| | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**)[d] | 55 | 2.7 | 94 (41/59) | 0 |
| | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**)[e] | 25 | 5.25 | 94 (19/81) | 0 |
| | [Ir(bpm)$(CO)_2$]$BPh_4$ (**3**) | 25 | 50 | 97 (30/70) | 0 |
| | [Ir(PyP)$(CO)_2$]$BPh_4$ (**9**)[e] | 25 | 3.3 | 96 (10/90) | 0 |
| | [Ir(PyP)(CO)Cl] (**11**) | 25 | 15.6 | 72 (23/77) | 0 |
| | [Rh(bim)$(CO)_2$]$BPh_4$ (**2**) | 25 | 70 | 85 (42/58) | 0 |
| | [Rh(bpm)$(CO)_2$]$BPh_4$ (**4**) | 25 | 1.5 | 27 (28/72) | 0 |
| | [Rh(PyP)$(CO)_2$]$BF_4$ (**10**)[e] | 25 | 7.1 | 94 (29/71) | 0 |
| | [Rh(PyP)(CO)Cl] (**12**) | 25 | 13.2 | 21 (24/76) | 0 |
| | No catalyst | 25 | 30 | 90 (20/80) | 0 |
| | | | | **14b** | **15b** |
| Propargyl alcohol (**13b**) | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**) | 55 | 18.5 | 87 (70/30) | 7[f] |
| | [Ir(bpm)$(CO)_2$]$BPh_4$ (**3**) | 55 | 12.5 | 34 (66/34) | 4[f] |
| | [Ir(PyP)(CO)Cl] (**11**) | 55 | 33 | 5 (60/40) | 5[f] |
| | [Rh(bim)$(CO)_2$]$BPh_4$ (**2**) | 55 | 24 | Trace | 0 |
| | [Rh(bpm)$(CO)_2$]$BPh_4$ (**4**) | 55 | 24 | Trace | 0 |
| | [Rh(PyP)(CO)Cl] (**12**) | 55 | 25 | 23 (56/44) | 15[f] |
| | No catalyst | 55 | 24 | Trace | 0 |
| | | | | **14c** | **15c** |
| 1-Pentyne (**13c**)[g] | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**) | 25 | 22 | Trace | 0 |
| | [Ir(bim)$(CO)_2$]$BPh_4$ (**1**)[e] | 40 | 44 | 4 (57/43) | 0 |
| | [Ir(bpm)$(CO)_2$]$BPh_4$ (**3**) | 25 | 22 | Trace | 0 |
| | [Ir(PyP)$(CO)_2$]$BPh_4$ (**9**)[e] | 40 | 18.6 | 97 (51/49) | 0 |
| | [Ir(PyP)(CO)Cl] (**11**) | 40 | 30 | 95 (44/56) | 0 |
| | [Rh(bim)$(CO)_2$]$BPh_4$ (**2**) | 25 | 24 | Trace | 0 |
| | [Rh(bpm)$(CO)_2$]$BPh_4$ (**4**) | 25 | 24 | Trace | 0 |
| | [Rh(PyP)$(CO)_2$]$BF_4$ (**10**)[e] | 40 | 26.5 | 84 (43/57) | 0 |
| | [Rh(PyP)(CO)Cl] (**12**) | 25 | 18 | Trace | 0 |
| | No catalyst | 25 | 25 | Trace | 0 |

[a] Reaction conditions: PhSH (0.13–0.15 mmol), alkynes (0.13–0.15 mmol), internal standard (dibromomethane or cyclohexane: 0.06–0.08 mmol), catalyst (1 mol%), THF-$d_8$ (0.5–0.6 mL). [b] Time as when no further significant formation of product(s) was observed. [c] Determined by $^1$H NMR. [d] 2 mol% catalyst. [e] Solvent = $CDCl_3$. [f] Conversion of the allylic alcohol to the corresponding aldehyde was observed. [g] For reactions at 25 °C no further formation of products were observed when temperature was increased to 40 °C.

products from hydrothiolation reactions, the intermolecular addition of the hydroxyl group into the terminal acetylene of two or more propargyl alcohol molecules was also observed giving a complex mixture of products including (**16**). The total conversions to product mixtures were approximately 90 and 54% for (**9**) and (**10**), respectively. While transition metal catalysed intramolecular addition of alkyn-ols to yield oxygen containing heterocycles is not uncommon,[2] this is one of a very few cases where the intermolecular addition of alcohol to alkynes has been reported.[39]




**16**

The *E*/*Z* ratios of the two anti-Markovnikov products formed on catalysis of the reaction between PhSH and the alkyne substrate was monitored using $^1$H NMR, and $Z \longrightarrow E$ isomerisation was observed for most reactions until an equilibrium mixture was obtained. On increasing the temperature, an increase in the equilibrium *E*/*Z* ratio was observed, indicating that the *Z* isomer is likely to be the kinetic product. For example, the reaction between PhSH and phenylacetylene catalysed by [Ir(bim)$(CO)_2$]$BPh_4$ (**1**) (2 mol%), at 55 °C (Fig. 3) clearly showed that isomer **14a**-*Z* isomerised to the *E* isomer **14a**-*E* as the reaction proceeded. Changing solvent from THF-$d_8$ to $CDCl_3$ did not have a significant effect on the overall yields of the reactions, but did appear to shift the equilibrium

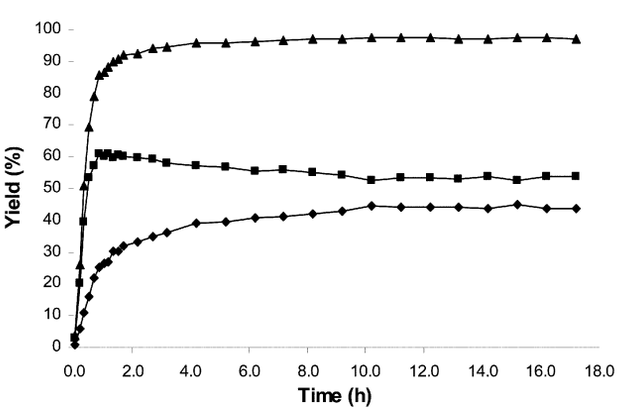
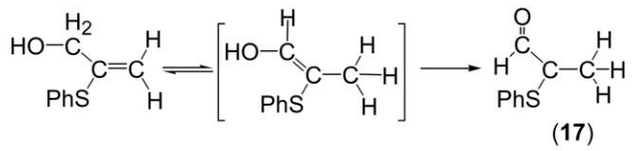



**Fig. 3** The time course of [Ir(bim)$(CO)_2$]$BPh_4$ (2 mol%) catalysed reaction between PhSH and phenylacetylene at 55 °C, showing the percentage conversion of starting material to products ((◆ = **14a**-*E*; ■ = **14a**-*Z*; ▲ = **14a** (**14a**-*E* + **14a**-*Z*)).

*E*/*Z* ratios of the anti-Markovnikov products in favour of the *Z* isomer.

The efficiency of the catalysed reactions was very dependent on the nature of the substrate. The general trend of reactivity observed was R = Ph– > $HOCH_2$– > $CH_3CH_2CH_2$– > $Me_3Si$–. The bulkiness of the $Me_3Si$– group might hinder the approach of (trimethylsilyl)acetylene to the metal centre. Thiophenol was shown to add to phenylacetylene smoothly in the absence of any metal catalyst giving exclusively the anti-Markovnikov

products, which possibly proceeded *via* a radical mechanism. During the course of the investigation we also observed the isomerisation–tautomerism of the allylic alcohol product (**15b**) to the aldehyde (**17**), which resulted from the Markovnikov addition of PhSH to propargyl alcohol (Scheme 5). Metal catalysed transposition of allylic alcohols into carbonyl compounds have been reviewed very recently.[40]




**Scheme 5**

## Conclusions

The novel bidentate P,N donor ligand, PyP (**5**) was synthesised, and a number of new cationic and neutral complexes of PyP (**5**) with iridium(I) and rhodium(I) $[M(PyP)(COD)]BPh_4$ (M = Ir (**6**); Rh (**7**)), $[Rh(PyP)(COD)]BF_4$ (**8**), $[Ir(PyP)(CO)_2]BPh_4$ (**9**), $[Rh(PyP)(CO)_2]BF_4$ (**10**), [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)) were also synthesised and characterised by NMR. The solid-state structures of (**6**), (**7**), (**11**) and (**12**) were determined by single-crystal X-ray diffraction analysis. The structures of both the neutral and charged complexes were similar, and showed a square-planar coordination around the metal centres, as expected for $d^8$ iridium(I) and rhodium(I). The conformation of the ligand bound to the metal centre was similar for all four complexes, forming a six-membered ring with a distorted boat conformation.

The efficiency of the complexes $[M(bim)(CO)_2]BPh_4$ (M = Ir (**1**), Rh (**2**)), $[M(bpm)(CO)_2]BPh_4$ [M = Ir (**3**), Rh (**4**)], $[Ir(PyP)(CO)_2]BPh_4$ (**9**), $[Rh(PyP)(CO)_2]BF_4$ (**10**) and [M(PyP)(CO)Cl] (M = Ir (**11**), Rh (**12**)) as catalysts for the addition of thiophenol to a number of terminal alkynes was variable. The iridium complexes were significantly more effective than their rhodium analogues in promoting hydrothioloation. Similarly, the complexes containing the P,N donor ligand PyP (**5**), were in most cases more effective as catalysts than the equivalent complexes with bidentate N-donor ligands. The cationic complexes with CO coligands are also found to be more effective than their neutral analogues. The successful transformations demonstrated good to excellent regioselectivity, with the anti-Markovnikov products as the predominant products. The *E*/*Z* isomeric ratios of the products formed was highly dependent on the nature of the alkynyl substrates.

This study reports, for the first time, the use of iridium complexes to effectively catalyse hydrothiolation. It is also the first time that rhodium(I) and iridium(I) complexes with bidentate N,N-donor and P,N-donor ligands have been utilised to facilitate metal catalysed reactions with thiols as substrates. Investigations currently underway into the mechanisms of this metal catalysed hydrothiolation will provide insight into the relative efficiencies of the catalyst.

## Experimental

All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk or vacuum techniques,[41] or in a nitrogen-filled dry box. The distillation of solvents was carried out under an atmosphere of nitrogen. Tetrahydrofuran (THF), diethyl ether, hexane, *n*-pentane and benzene were distilled from sodium, benzophenone. Dichloromethane and acetonitrile were dried by distillation from calcium hydride. Methanol was distilled from dimethoxymagnesium. THF-$d_8$ was dried as for its protonated analogue, $CDCl_3$ used in catalysis was dried over calcium hydride, degassed *via* three cycles of freeze–pump–thaw, then vacuum distilled and stored under vacuum.

All compressed gases were obtained from British Oxygen Company (BOC gases) and Linde Gas Pty. Ltd. Nitrogen (>99.5%) and carbon monoxide (>99.5%) were used as supplied without purification. Pyrazole, 1,2-dibromoethane, tetrabutylammonium bromide, *n*-butyllithium (1.6 M solution in hexane), 1,5-cyclooctadiene (COD), sodium tetraphenylborate, sodium tetrafluoroborate, *cis*-cyclooctene (COE) were obtained from Aldrich and used without further purification. Thiophenol, phenylacetylene, (trimethylsilyl)acetylene, 1-pentyne, propargyl alcohol, dibromomethane, dichloromethane, cyclohexane used in hydrothiolation reactions were purchased from Aldrich, dried by standard methods[42] and degassed *via* three cycles of freeze–pump–thaw prior to use. Iridium(III) chloride hydrate, rhodium(III) chloride hydrate were obtained from Precious Metals Online PMO P/L and were used without further purification. $[Ir(COD)(\mu\text{-}Cl)]_2$,[43] $[Rh(COD)(\mu\text{-}Cl)]_2$,[44] $[Rh(CO)_2(\mu\text{-}Cl)]_2$,[45] $[Ir(COE)_2(\mu\text{-}Cl)]_2$,[43] diphenylphosphine[46] were prepared by literature methods. Complexes $[M(bim)(CO)_2]BPh_4$ (M = Ir (**1**), Rh, (**2**))[17] and $[Rh(bpm)(CO)_2]BPh_4$ (**4**)[17b] were synthesised by Dr Vicki Tolhurst using literature methods. $[Ir(bpm)(CO)_2]BPh_4$ (**3**) was also synthesised following a literature method.[19]

The $^1H$, $^{31}P$, $^{13}C$ NMR spectra were recorded on Bruker DPX300, DMX500 spectrometers, operating at 300 and 500 MHz ($^1H$); 121, 202 MHz ($^{31}P$); 75, 125 MHz ($^{13}C$). All the spectra were recorded at 298 K unless specified. $^1H$ NMR and $^{13}C$ NMR chemical shifts were referenced internally to residual solvent resonances. $^{31}P$ NMR was referenced externally using $H_3PO_4$ (85% in $D_2O$) in a capillary.

MS, GC-MS was done in the Mass Spectrometry Unit, School of Chemical Sciences, the University of New South Wales. ES-MS was performed by Dr Keith Fisher at the University of Sydney. HRMS was done at the Research School of Chemistry, the Australian National University. Melting points were recorded using a Reichert or Mel-Temp apparatus and are uncorrected. IR spectra were recorded using an ATI Mattson Genesis Series F.T.I.R. spectrometer. Elemental analyses were done at the Campbell Microanalytical Laboratory at the University of Otago, New Zealand. Single-crystal X-ray structure analyses were done at the X-ray Crystallography Centre, the University of Sydney, Australia.

### Synthesis of $[Ir(bim)(CO)_2]BPh_4$ (1)

Solutions of bis(1-methylimidazol-2-yl)methane, bim (252 mg, 1.43 mmol) in methanol (5 mL) and sodium tetraphenylborate (548 mg, 1.6 mmol) in methanol (5 mL) were added to a solution of $[Ir(COD)(\mu\text{-}Cl)]_2$ (457 mg, 0.68 mmol) in methanol (20 mL) and hexane (5 mL) at room temperature. The mixture was stirred for 2 h and then placed under an atmosphere of carbon monoxide gas for three days, during which time a pale yellow solid formed. The solid was isolated by filtration and washed with hexane and methanol. Recrystallisation from acetone afforded orange crystals of (bis(*N*-methylimidazol-2-yl)methane)dicarbonyliridium(I) tetraphenylborate (**1**) (895 mg, 89%), mp 190–193 °C (decomp.).

ES-MS (tetrahydrofuran) ($ES^+$): *m*/*z* 425 ($[Ir(bim)(CO)_2]^+$, 100%). Found: C, 56.5; H, 4.6; N, 7.4. $C_{35}H_{32}BIrN_4O_2$ requires: C, 56.53; H, 4.34; N, 7.53%. $^1H$ NMR (THF-$d_8$): $\delta$ 7.35 (d, 2H, $^3J$ = 1.7 Hz, H4), 7.30–7.27 (m, 8H, *o*-CH of $BPh_4$), 7.16 (d, 2H, H5), 6.80 (m, 8H, *m*-CH of $BPh_4$), 6.66 (m, 4H, *p*-CH of $BPh_4$), 3.67 (s, 2H, $CH_2$), 3.23 (s, 6H, N–$CH_3$) ppm. $^{13}C\{^1H\}$ NMR (THF-$d_8$): $\delta$ 174.0 (Ir–CO), 165.7–164.2 (m, *ipso*-C of $BPh_4$), 143.3 (C2), 137.1 (*o*-C of $BPh_4$), 131.5 (C4), 125.9 (*m*-C of $BPh_4$), 124.7 (C5), 122.1 (*p*-C of $BPh_4$), 34.3 (N-$CH_3$), 24.1 ($CH_2$) ppm. IR (KBr disc): $\nu$ 2084 (CO), 2014 (CO) $cm^{-1}$.

### Synthesis of 1-(2-diphenylphosphinoethyl)pyrazole, PyP (12)

**(a) Synthesis of 1-(2-bromoethyl)pyrazole.** 1-(2-bromoethyl)-pyrazole was synthesised by the following modifications of a

literature procedure.[30] 1,2-Dibromoethane (215 mL, 2.5 mol) was added to a mixture of pyrazole (6.81g, 100 mmol), sodium hydroxide solution (40% (w/v), 30 mL), tetrabutylammonium bromide (3.22 g, 10 mmol). The reaction was vigorously stirred for 24 h at room temperature. Water (60 mL) was added to the reaction mixture and the organic layer was separated, washed with water (75 mL) and dried over anhydrous calcium chloride. After filtration, the solvent was removed in *vacuo* to give a pale yellow oil. The product, 1-(2-bromoethyl)pyrazole was collected as a colourless liquid on vacuum distillation (14.32 g, 82%), bp 80–82 °C/2 mmHg (lit.[47] 65–66 °C/0.5 mmHg).

$^1$H NMR (300 MHz; $CDCl_3$): $\delta$ 7.55 (d, 1H, $^3J$ = 1.6, H3), 7.46 (d, 1H, $^3J$ = 2.4, H5), 6.25 (dd apparent t, 1H, $^3J$ = 2.0, H4), 4.5 (t, 2H, $^3J$ = 6.5, N–$CH_2$), 3.72 (t, 2H, $^3J$ = 6.5, Br–$CH_2$) ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CDCl_3$): $\delta$ 140.6 (C3), 130.4 (C5), 105.9 (C4), 53.3 (N–$CH_2$), 30.2 (Br–$CH_2$) ppm.

**(b) Synthesis of 1-(2-diphenylphosphinoethyl)pyrazole, PyP (5).** *n*-Butyllithium (1.6 M in hexane, 13.8 mL, 22.1 mmol) was added dropwise into a solution of diphenylphosphine (3.54 mL, 20.4 mmol) in tetrahydrofuran (THF, 30 mL) at 0 °C. The bright red solution of lithium diphenylphosphide was stirred at this temperature another hour. This solution was transferred slowly *via* a cannula into a solution of 1-(2-bromoethyl)-pyrazole (3.57 g, 20.4 mmol) in THF (60 mL) at 0 °C. The resulting pale yellow solution was stirred for 90 min at 0 °C and at room temperature for 4 h.The solvent was then removed under *vacuo,* benzene (70 mL) was added and the organic layer was washed twice with deoxygenated water (2 × 25 mL), dried over magnesium sulfate, filtered and the solvent was removed in *vacuo* to give very pale yellow oil. Methanol (5 mL) was added to the oil and the resulting solution was placed in a freezer (−20 °C) over night. A white precipitate formed and was collected by filtration, washed with ice cold methanol (3 × 2 mL) and dried in *vacuo*. 1-(2-diphenylphosphinoethyl)-pyrazole (**5**) was collected as a white waxy solid (4.47 g, 78.1%), mp 48–50 °C

HRMS: found: *m*/*z* 280.112679; $C_{17}H_{17}N_2P$ requires 280.112937. Found: C, 72.81; H, 6.11; N: 10.33. $C_{17}H_{17}N_2P$ requires: C, 72.84; H, 6.11; N, 9.99%. $^1$H NMR (300 MHz, benzene-$d_6$): $\delta$ 7.58 (d, 1H, $^3J$ = 1.8, H3), 7.35–7.30 (m, 4H, *o*-CH of $PPh_2$), 7.08–7.03 (m, 6H, *m*-CH and *p*-CH of $PPh_2$), 6.77 (d, 1H, $^3J$ = 2.3, H5), 6.03 (dd apparent t, 1H, $^3J$ = 2.0, H4), 3.95 (m, 2H, N–$CH_2$), 2.49 (m, 2H, P–$CH_2$) ppm. $^{31}$P NMR (121 MHz, benzene-$d_6$): $\delta$ −20.98 ppm. $^{13}$C NMR (75 MHz, benzene-$d_6$): $\delta$ 140.2 (C3), 139.0 (d, $^1J$(P–C) = 13.7, *ipso*-C of $PPh_2$), 133.7 (d, $^2J$(P–C) = 19.4, *o*-C of $PPh_2$), 129.6 (*p*-C of $PPh_2$), 129.5 (d, $^3J$(P–C) = 6.6, *m*-C of $PPh_2$), 129.2 (C5), 106.0 (C4), 50.0 (d, $^2J$(P–C) = 25.0, N–$CH_2$), 30.6 (d, $^1J$ = 14.7, P–$CH_2$) ppm. IR (KBr disc): *v* 3151, 3116, 3087, 2927, 1511, 1490, 1463, 1447, 1429, 1395, 1365, 1321, 1304, 1285, 1257, 1204, 1130, 1090, 1066, 1042, 1028, 987, 965, 948, 784, 761, 742, 701, 698 cm$^{-1}$

### Synthesis of [Ir(PyP)(COD)]$BPh_4$ (6)

Methanol (30 mL) was added to a mixture of $[Ir(COD)(\mu\text{-}Cl)]_2$ (0.336 g, 0.50 mmol), PyP (**5**) (0.280 g, 1.00 mol) and sodium tetraphenylborate (0.376, 1.10 mmol). The suspension was degassed *via* three freeze–pump–thaw cycles. The reaction was the allowed to stir at RT overnight. The solvent was half reduced in *vacuo*. The product was collected by filtration, washed with methanol (6 × 4 mL) and dried under vacuum to give an orange solid (0.833 g, 93%), mp 185–186 °C (decomp.).

ES-MS (MeOH): ($ES^+$): *m*/*z* 581.2 ([Ir(PyP)(COD)]$^+$, 100%); ($ES^-$): *m*/*z* 319.6 ($BPh_4^-$, 100%). Found: C, 64.80; H, 5.40; N, 3.26. $C_{49}H_{49}N_2PIrB$ requires: C, 65.40; H, 5.49, N, 3.11%. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.56 (d, 1H, $^3J$ = 2.3, H3), 7.54–7.40 (m, 10H, CH of $PPh_2$), 7.39–7.33 (br m, 8H, *o*-CH of $BPh_4$), 7.20 (d, 1H, $^3J$ =2.4, H5), 7.03 (t, 8H, $^3J$ = 7.2, *m*-CH of $BPh_4$), 6.88 (t, 4H, $^3J$ = 7.2, *p*-CH of $BPh_4$), 6.32 (dd apparent t, 1H, $^3J$ = 2.3, H4), 4.95 (br, 2H, CH (*trans* to P) of COD), 4.29 (m, 2H, N–$CH_2$), 3.19 (br, 2H, CH of COD (*cis* to P)), 2.44 (m, 2H, P–$CH_2$), 2.39–2.22 (br, 4H, CH*H* (2H, *trans* to P) and CH*H* (2H, *cis* to P) of COD), 2.17–1.93 (br, 4H, C*H*H (2H, *trans* to P) and C*H*H (2H, *cis* to P) of COD) ppm. $^{31}$P NMR (121 MHz, $CD_2Cl_2$): $\delta$ 10.50 ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 163.9 (q, $^1J$(B–C) = 49.4, *ipso*-C of $BPh_4$), 141.6 (C3), 135.8 (*o*-C of $BPh_4$), 134.7 (C5), 133.1 (d, *J*(P–C) = 10.9, *o*-C or *m*-C of $PPh_2$), 131.4 (d, $^4J$(P–C) = 2.2, *p*-CH of $PPh_2$), 129.5 (d, $^1J$(P–C) = 54.3, *ipso*-C of $PPh_2$), 129.1 (d, *J*(P–C) = 10.2, *m*-C or *o*-C of $PPh_2$), 125.6 (q, $^4J$(B–C) = 2.9, *m*-C of $BPh_4$), 121.7 (*p*-C of $BPh_4$), 108.0 (C4), 95.3 (d, $^3J$(P–C) = 11.6, CH (*trans* to P) of COD), 64.1 (d, CH (*cis* to P) of COD), 51.4 (d, $^2J$(P–C) = 2.9, N–$CH_2$), 32.4 (d, $^3J$(P–C) = 2.9, $CH_2$ of COD), 29.4 (d, $^3J$(P–C) = 2.2, $CH_2$ of COD), 27.2 (d, $^1J$(P–C) = 32.7, P–$CH_2$) ppm. IR (KBr disc): *v* 3107, 3054, 2983, 1579, 1478, 1434, 1283, 1178, 1100, 1075, 1030, 998, 843, 744, 734, 705, 613, 530, 491, 439 cm$^{-1}$.

### Synthesis of [Rh(PyP)(COD)]$BPh_4$ (7)

A solution of PyP (**5**) (0.140 g, 0.50 mmol) in tetrahydrofuran (5 mL) was added to a solution of $[Rh(COD)Cl]_2$ (0.148 g, 0.3 mmol) in THF (10 mL). After allowing the reaction to stir for 30 min, sodium tetraphenylborate (0.171 g, 0.5 mmol) was added and the solution was stirred for another 30 min. Diethyl ether (50 mL) was added to precipitate the product. The solid was collected by filtration, washed with methanol (3 × 4 mL) and dried in *vacuo* to afford [Rh(PyP)(COD)]$BPh_4$ as a bright yellow solid (0.376 g, 93%) mp 154–156 °C (decomp.).

ES-MS (MeOH–DCM): ($ES^+$): *m*/*z* 491.1 ([Rh(PyP)-(COD)]$^+$, 100%); ($ES^-$): *m*/*z* 319.7 ($BPh_4^-$, 100%). Found: C, 72.38; H, 5.94; N, 3.50. $C_{49}H_{49}BN_2PRh$ requires: C, 72.60; H, 6.09; N, 3.46%. $^1$H NMR (500 MHz, $CD_2Cl_2$): $\delta$ 7.53–7.42 (m, 10H, CH of $PPh_2$), 7.39 (d, 1H, $^3J$ = 2.1, H3), 7.35 (br m, 8H, *o*-CH of $BPh_4$), 7.19 (d, 1H, $^3J$ = 2.3, H5), 7.02 (8H, $^3J$ = 7.2, *m*-CH of $BPh_4$), 6.87 (t, 4H, $^3J$ = 7.2, *p*-CH of $BPh_4$), 6.21 (dd apparent t, 1H, $^3J$ = 2.2, H4), 5.28 (br, 2H, CH (*trans* to P) of COD), 4.36 (m, 2H, N–$CH_2$), 3.50 (br, 2H, CH (*cis* to P) of COD), 2.54–2.41 (br m, 4H, C*H*H (2H, *trans* to P), C*H*H (2H, *cis* to P) of COD), 2.36 (m, 2H, P–$CH_2$), 2.26 (br m, 2H, CH*H* (*trans* to P) of COD), 2.20 (br m, 2H, CH*H* (*cis* to P) of COD) ppm. $^{31}$P NMR (121 MHz, $CD_2Cl_2$): $\delta$ 25.2 (d, $^1J$(Rh–P) = 148.6) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 164.3 (q, $^1J$(B–C) = 49.9, *ipso*-C of $BPh_4$), 142.0 (C3), 136.3 (*o*-C of $BPh_4$), 134.3 (C5), 133.3 (d, *J*(P–C) = 11.0, *m*-C or *o*-C of $PPh_2$), 131.8 (d, $^4J$(P–C) = 2.0, *p*-C of $PPh_2$), 130.3 (d, $^1J$(P–C) = 45.9, *ipso*-C of $PPh_2$), 129.5 (d, *J*(P–C) = 10.0, *o*-C or *m*-C of $PPh_2$), 126.0 (q, $^3J$(B–C) = 2.0, *m*-CH of $BPh_4$), 122.1 (*p*-C of $BPh_4$), 108.1 (C4), 106.9 (dd, *J*(Rh–C or P–C) = 10.0 or 7.0, CH (*trans* to P) of COD), 79.1 (d, $^1J$(Rh–C) = 12.0, CH (*cis* to P), of COD), 51.7 (d, $^2J$(P–C) = 6.0, N–$CH_2$), 32.5 ($CH_2$ (*cis* to P) of COD), 29.2 ($CH_2$ (*trans* to P) of COD), 28.6 (d, $^1J$(P–C) = 25.9, P–$CH_2$) ppm. IR (KBr disc): *v* 3054, 3041, 3027, 2997, 2981, 1651, 1633, 1578, 1478, 1455, 1436, 1424, 1410, 1384, 1178, 1149, 1129, 1109, 1100, 1071, 1030, 842, 779, 744, 734, 705, 669, 676, 613, 523 cm$^{-1}$.

### Synthesis of [Rh(PyP)(COD)]$BF_4$ (8)

A solution of PyP (**5**) (0.140g, 0.50 mmol) in THF (10 mL) was added dropwise into a solution of $[Rh(COD)(\mu\text{–}Cl)]_2$ (0.131 g, 0.26 mmol) in THF (20 mL) under an atmosphere of nitrogen. When the addition was completed the reaction was stirred for another 20 min, and sodium tetrafluoroborate (0.055 g, 0.50 mmol) was added. The reaction was stirred for a further 20 min. Most of the solvent was removed in *vacuo* until about 5 mL of solvent was left in the reaction flask. Diethyl ether (30 mL) was added to precipitate the solid product. The bright yellow product was collected by filtration, washed with methanol

(3 × 0.5 mL), *n*-pentane (2 × 4 mL) and dried *in vacuo*. Yield (0.260 g, 90%) mp 185–187 °C (decomp.)

ES-MS (MeOH) ($ES^+$): *m/z* 491.2 ($[Rh(PyP)(COD)]^+$, 100%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.75 (d, 1H, $^3J$ = 2.3, H3/H5), 7.54–7.44 (m, 11H, $PPh_2$ and H5/H3), 6.32 (dd apparent t, $^3J$ = 2.2, H4), 5.35 (br, 2H, CH (*trans* to P) of COD), 5.05 (m, 2H, N–$CH_2$), 3.58 (br, 2H, CH (*cis* to P) of COD), 2.77 (m, 2H, P–$CH_2$), 2.51 (br m, 4H, $CH_2$ of COD), 2.26 (br m, 4H, $CH_2$ of COD) ppm. $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ 25.6 (d, $^1J$(Rh–P) = 148.9) ppm. IR (KBr disc): *v* 2985, 2976, 1649, 1438, 1072, 1059, 1034 (last three $BF_4$), 773, 705, 525 $cm^{-1}$.

### Synthesis of [Ir(PyP)(CO)$_2$]BPh$_4$ (9)

Carbon monoxide was bubbled through a suspension of [Ir(PyP)(COD)]$BPh_4$ (**5**) (0.187 g, 0.208 mmol) in *n*-pentane (15 mL), methanol (3 mL) for 1 hour during which time the colour of the solid changed from bright orange to bright yellow. The product was collected by filtration, washed with *n*-pentane (4 × 3 mL) and dried in under vacuum. [Ir(PyP)$(CO)_2$]$BPh_4$ (**9**) was collected as a bright yellow solid 0.146 g, 83%; mp 131–133 °C (decomp.).

Found: C, 60.32; H, 4.23; N, 3.42. $C_{43}H_{37}BIrN_2O_2P$ requires: C, 60.92; H, 4.40; N, 3.30%. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 7.80 (d, $^3J$ = 2.4, H3/H5), 7.67–7.46 (m, 10H, CH of $PPh_2$), 7.35 (br m, 8H, *o*-CH of $BPh_4$), 6.98 (t, $^3J$ = 7.2, *m*-CH of $BPh_4$ and H5/H3), 6.39 (dd apparent t, $^3J$ = 2.3, H4), 3.67 (m, 2H, N–$CH_2$), 2.24 (m, 2H, P–$CH_2$) ppm. $^{31}$P NMR (121 MHz, acetone-$d_6$): $\delta$ 15.4 ppm. IR (KBr disc): *v* 2085w (C≡O), 2060s (C≡O), 2022s (C≡O), 1982w (C≡O) $cm^{-1}$

### Synthesis of [Rh(PyP)(CO)$_2$]BF$_4$ (10)

Hexane (10 mL) and methanol (1 mL) were added to [Rh(PyP)-(COD)]$BF_4$ (**8**) (0.070g, 0.12 mmol) under an atmosphere of nitrogen. The reaction mixture was degassed *via* two cycles of freeze–pump–thaw. The reaction was then put under an atmosphere of carbon monoxide for 3 h. The colour of the solid changed from bright yellow to pale yellow. The solid was collected by filtration, washed with methanol (2 × 0.3 mL), *n*-pentane (3 × 2 mL) and dried in *vacuo* to afford [Rh(PyP)-$(CO)_2$]$BF_4$ (0.057g, 89%), mp 210–213 °C (decomp.).

ES-MS (MeOH) ($ES^+$): *m/z* 411.3 ($[Rh(PyP)(CO)]^+$, 18), 443.0 ($[Rh(PyP)(CO)(MeOH)]^+$, 57), 793.1 (44), 857.1 (100%). $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 8.54 (d, $^3J$ = 2.3, H3/H5), 7.85–7.79 (m, 4H, CH of $PPh_2$), 7.52–7.49 (m, 7H, CH of $PPh_2$ and H5/H3), 6.31 (dd apparent t, $^3J$ = 2.2, H4), 4.51 (m, 2H, N–$CH_2$), 2.67 (m, 2H, P–$CH_2$) ppm. $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ 38.7 (d, $^1J$(Rh–P) = 165.6) ppm. IR (KBr disc): *v* 2002s (CO), 1995s (CO), 1951w (CO) $cm^{-1}$

### Synthesis of [Ir(PyP)(CO)Cl] (11)

Acetonitrile (50 mL) was added to a three-necked round bottom flask containing $[Ir(COE)_2(\mu\text{-}Cl)]_2$ (0.222g, 0.25 mmol) under an atmosphere of nitrogen. After the suspension was stirred for 15 min, nitrogen was replaced by carbon monoxide. The remaining solid $[Ir(COE)_2(\mu\text{-}Cl)]_2$ dissolved almost immediately to form a pale yellow solution. After stirring under carbon monoxide for 5 min carbon monoxide was replaced by nitrogen and PyP (**5**) (0.140 g, 0.5 mmol) in acetonitrile (10 mL) was added slowly to the pale yellow solution. After stirring at room temperature for 15 min, most of the solvent was removed until there was about 5 mL left. A yellow precipitate formed on removal of about 20% of the acetonitrile. The precipitate was collected by filtration, washed with acetonitrile (3 × 3 mL) and dried *in vacuo* to give a pale yellow powder. Recrystallisation from dichloromethane/hexane afforded pale yellow needle-like crystals of [Ir(PyP)(CO)Cl] (**11**) (0.240 g, 90%) mp 235–236 °C (decomp.).

Found: C, 40.42; H, 3.13; N, 5.14. $C_{18}H_{17}ClIrN_2OP$ requires: C, 40.34; H, 3.20; N, 5.23%. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 8.50 (d, 1H, $^3J$ = 2.3, H3), 7.82–7.78 (m, 4H, *o*-CH of $PPh_2$), 7.56 (d, 1H, $^3J$ = 2.3, H5), 7.51–7.47 (m, 6H, *m*-CH and *p*-CH of $PPh_2$), 6.73 (dd apparent t, 1H, $^3J$ = 2.3, H4), 4.59 (m, 2H, N–$CH_2$), 2.74 (m, 2H, P–$CH_2$) ppm. $^{31}$P{$^1$H} NMR (121 MHz, $CD_2Cl_2$): $\delta$ 10.43 ppm. $^{13}$C{$^1$H} NMR (75 MHz, $CD_2Cl_2$): $\delta$ 174.4 (d, $^3J$(P–C) = 13.8, CO), 144.0 (C3), 133.6 (C5), 133.2 (d, $^1J$(P–C) = 61.8, *ipso*-C of $PPh_2$), 132.9 (d, $^2J$(P–C) = 10.9, *o*-C of $PPh_2$), 130.8 (d, $^4J$(P–C) = 2.5, *p*-C of $PPh_2$), 128.5 (d, $^3J$(P–C) = 10.9, *m*-C of $PPh_2$), 105.9 (C4), 49.0 (d, $^2J$(P–C) = 2.2, N–$CH_2$), 27.1 (d, $^1J$(P–C) = 34.9, P–$CH_2$) ppm. IR (KBr disc): *v* 1983s (CO), 1961w (CO) $cm^{-1}$.

### Synthesis of [Rh(PyP)(CO)Cl] (12)

A solution of 1-(2-diphenylphosphinoethyl)pyrazole, PyP (**5**) (0.175 g, 0.62 mmol) in methanol (8 mL) was added slowly to a solution of $[Rh(CO)_2(\mu\text{-}Cl)]_2$ (0.130 g, 0.33 mmol) in methanol (15 mL) under an atmosphere of nitrogen. A yellow precipitate formed during the addition. The reaction was stirred for another 30 min at RT. The precipitate was filtered off and washed with methanol (4 × 3 mL) and dried in *vacuo*. [Rh(PyP)(CO)Cl] (**12**) was collected as a yellow solid (0.268g, 96%), mp 231–232 °C (decomp.)

Found: C, 48.41; H, 4.08; N, 6.20. $C_{18}H_{17}ClN_2OPRh$ requires C, 48.40; H, 3.84; N, 6.27%. $^1$H NMR (300 MHz, $CD_2Cl_2$): $\delta$ 8.47 (d, 1H, $^3J$ = 2.3, H3), 7.87–7.79 (m, 4H, *o*-CH of $PPh_2$), 7.53–7.47 (m, 7H, *m*-CH, *p*-CH of $PPh_2$ and H5), 6.32 (dd apparent t, 1H, $^3J$ = 2.2, H4), 4.51 (m, 2H, N–$CH_2$), 2.67 (m, 2H, P–$CH_2$) ppm. $^{31}$P NMR (121 MHz, $CD_2Cl_2$): $\delta$ 38.68 (d, $^1J$(Rh–P) = 165.5) ppm. $^{13}$C NMR (75 MHz, $CD_2Cl_2$): $\delta$ 188.7 (dd, $^1J$(Rh–C) = 71.2, $^2J$(P–C) = 18.2, CO), 144.4 (C3), 133.7 (dd, $^1J$(P–C) = 52.3, $^2J$(Rh–C) = 2.0, *ipso*-C of $PPh_2$), 133.2 (C5), 132.9 (dd, $^2J$(P–C) = 11.6, $^3J$(Rh–C) =1.5, *o*-C of $PPh_2$), 130.9 (d, $^4J$(P–C) = 2.2, *p*-C of $PPh_2$), 128.7 (d, 128.7 (d, $^3J$(P–C) = 10.9, *m*-C of $PPh_2$), 105.6 (C4), 48.0 (N–$CH_2$), 28.0 (d, $^1J$(P–C) = 26.9, P–$CH_2$) ppm. IR (KBr disc): *v* 1995s (CO), 1951w (CO) $cm^{-1}$.

### General procedure for catalytic hydrothiolation

All the metal complex catalysed hydrothiolation reactions were performed on a small scale in NMR tubes fitted with a concentric Teflon valve Youngs top with THF-$d_8$ or $CDCl_3$ (0.5–0.6 mL) as solvents. The metal complex (1 mol%, 1.2–1.5 μmol, 0.8–0.9 mg for neutral complexes and (**10**), 1.1–1.4 mg for other cationic complexes) was placed in an NMR tube, and solvent was distilled into the tube on a high vacuum line. The Teflon valve was replaced by a rubber septum in a nitrogen-filled dry box. Internal standard (dichloromethane, dibromomethane, or cyclohexane, 50 mol%, 0.06–0.09 mmol) and alkyne substrate (phenylacetylene (**13a**), propargyl alcohol (**13b**), 1-pentyne (**13c**), (trimethylsilyl)acetylene (**13d**), 0.12–0.15 mmol) were injected into the tube using a microsyringe. After a $^1$H NMR spectrum was recorded, the sample was frozen and thiophenol (0.12–0.15 mmol, 1 equivalent to the alkyne substrate) was added. Zero time was taken as the time when the sample was warmed to the desired reaction temperature. Reaction progress was monitored by acquiring $^1$H NMR at regular intervals. Percentage conversion was determined by integration of the $^1$H NMR spectra, and calculated based on the amount of the limiting reagent. Resonances attributed to the products and substrates were integrated against an internal standard (known quantity), or relative to each other in cases when an internal standard was not used. In most cases, the identities of the products were confirmed by subjecting the reaction mixtures to GC-MS after filtering through a plug of silica gel.

### X-Ray crystal analysis

Single-crystal diffraction data for compounds (**6**), (**7**), (**11**) and (**12**) were obtained with a Bruker SMART 1000 CCD

diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube. Data for (**11**) and (**12**) were collected at room temperature, and data for (**6**) and (**7**) were collected at 150(2) K. The data integration and reduction were undertaken with SAINT and XPREP,[48] and subsequent computations were carried out with the teXsan,[49] WinGX[50] and XTAL[32] graphical user interfaces. A Gaussian absorption correction[51,48] was applied to the data; there was no evidence of crystal decay. The structures were solved by direct methods with SIR97,[52] and extended and refined with SHELXL-97.[53] In general the non-hydrogen atoms were modeled with anisotropic displacement parameters and a riding atom model was used for the hydrogen atoms. The four alkene hydrogen atom sites of (**6**) and (**7**) were located and modeled with isotropic displacement parameters. ORTEP[31] depictions of the molecules with 20% displacement ellipsoids are provided in Figs. 1 and 2. The structures of (**6**) and (**7**) were obtained in the non-centrosymmetric space group *Fdd*2 (no. 43), and the absolute structures were established with the Flack[54] parameter refining to 0.000(3) and 0.000(12). respectively.

CCDC reference numbers 2007600–207603.

See http://www.rsc.org/suppdata/dt/b3/b303774f/ for crystallographic data in CIF or other electronic format.

## Acknowledgements

We gratefully acknowledge financial support from the University of New South Wales and the Australian Government for an International Postgraduate Research Scholarship (K. Q. V.) and Australian Postgraduate Award (S. B.). We thank Dr Vicki Tolhurst for the synthesis of compounds (**1**), (**2**) and (**4**).

## References

1 (*a*) F. Pohlki and S. Doye, *Chem. Soc. Rev.*, 2003, **32**, 104–114; (*b*) M. Nobis and D. Drießen-Hölscher, *Angew. Chem., Int. Ed.*, 2001, **40**, 3983–3985; (*c*) G. A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161–2185; (*d*) T. Müller and M. Beller, *Chem. Rev.*, 1998, **98**, 675–703; (*e*) R. Taube, in *Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook*, ed. B. Cornils and W. A. Herrmann, Wiley-VCH, Weinheim, Germany, 2000, pp. 507—520; and references therein.

2 (*a*) B. Weyershausen and K. H. Dötz, *Eur. J. Inorg. Chem.*, 1999, 1057–1066; (*b*) R.-S. Liu, *Pure Appl. Chem.*, 2001, **73**, 265–269 and references therein.

3 J. B. Press, *Chem. Heterocycl. Compd.*, 1991, **44**, 397–502.

4 J. March, *Advanced Organic Chemistry*, J. Wiley and Sons, New York, 4th edn., 1992.

5 (*a*) L. L. Hegedus and R. W. McCabe, *Catalyst Poisoning*, Marcel Dekker, New York, 1984; (*b*) A. T. Hutton, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, VCH, Weinheim, 1996, vol. 2, p. 969; (*c*) M. R. Dubois, *Chem. Rev.*, 1989, **89**, 1–9.

6 T. Kondo and T. Mitsudo, *Chem. Rev.*, 2000, **100**, 3205–3220.

7 (*a*) K. Griesbaum, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 273–287; (*b*) D. Crich, in *Organosulfur Chemistry: Synthetic Aspects*, ed. P. Page, Academic Press, London, 1999, p. 49–88.

8 J. W. McDonald, J. L. Corbin and W. E. Newton, *Inorg. Chem.*, 1976, **15**, 2056–2061.

9 (*a*) A. Ogawa, T. Ikeda, K. Kimura and T. Hirao, *J. Am. Chem. Soc.*, 1999, **121**, 5108–5114; (*b*) A. Ogawa, *J. Organomet. Chem.*, 2000, **611**, 463–474.

10 A. Ogawa, J.-i. Kawakami, N. Sonoda and T. Hirao, *J. Org. Chem.*, 1996, **61**, 4161–4163.

11 L.-B. Han and M. Tanaka, *Chem. Commun.*, 1999, 395–402.

12 H. Kuniyasu, A. Ogawa, K.-I. Sato, I. Ryu, N. Kambe and N. Sonoda, *J. Am. Chem. Soc.*, 1992, **114**, 5902–5903.

13 J.-E. Bäckvall and A. Ericsson, *J. Org. Chem.*, 1994, **59**, 5850–5851.

14 U. Koelle, Chr. Rietmann, J. T. Wagner and U. Englert, *Organometallics*, 1995, **14**, 703–713.

15 (*a*) F. E. McDonald, *Chem. Eur. J.*, 1999, **5**, 3103–3106; (*b*) F. E. McDonald, S. A. Burova and L. G. Huffman, Jr., *Synthesis*, 2000, **7**, 970–974.

16 A. Togni and L. M. Venanzi, *Angew. Chem., Int. Ed.*, 1994, **33**, 497–526.

17 (*a*) S. Burling, L. D. Field and B. A. Messerle, *Organometallics*, 2000, **19**, 87–90; (*b*) S. Burling, Ph.D. Thesis, University of Sydney, 2001.

18 S. Elgafi, L. D. Field and B. A. Messerle, *J. Organomet. Chem.*, 2000, **607**, 97–104.

19 L. D. Field, B. A. Messerle, M. Rehr, L. P. Soler and T. W. Hambley, *Organometallics*, 2003, **22**, 2387–2395.

20 C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233–350.

21 (*a*) P. Espinet and K. Soulantica, *Coord. Chem. Rev.*, 1999, **193–195**, 499–556 and references therein; (*b*) G. R. Newkome, *Chem. Rev.*, 1993, **93**, 2067–2089 and references therein.

22 K. N. Gavrilov and A. I. Poloukhin, *Russ. Chem. Rev.*, 2000, **8**, 661–682 and references therein.

23 (*a*) H. Yang, N. Lugan and R. Mathieu, *C. R. Acad. Sci. Ser. IIC2 4*, 1999, 251–258; (*b*) J. T. Mague and J. L. Krinsky, *Inorg. Chem.*, 2001, **40**, 1962–1971; (*c*) M. P. Anderson, C. C. Tso, B. M. Mattson and L. H. Pignolet, *Inorg. Chem.*, 1983, **22**, 3267–3275; (*d*) M. P. Anderson, A. L. Casalnuovo, B. J. Johnson, B. M. Mattson, A. M. Mueting and L. H. Pignolet, *Inorg. Chem.*, 1988, **27**, 1649–1658.

24 (*a*) P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680–699 and references therein; (*b*) G. Helmchen and A. Pfaltz, *Acc. Chem. Res.*, 2000, **33**, 336–345 and references therein; (*c*) D.-R. Hou, J. H. Relbenspies and K. Burgess, *J. Org. Chem.*, 2001, **66**, 206–215; (*d*) D. G. Blackmond, A. Lightfoot, A. Pfaltz, T. Rosner, P. Schnider and N. Zimmermann, *Chirality*, 2000, **4**, 442–449; (*e*) P. Dotta, A. Magistrato, U. Rothlisberger, P. S. Presgosin and A. Albinati, *Organometallics*, 2002, **21**, 3033–3041; (*f*) S. Kainz, A. Brinkmann, W. Leitner and A. Pfaltz, *J. Am. Chem. Soc.*, 1999, **121**, 6421–6429; (*g*) D.-R. Hou and K. Burgess, *Org. Lett.*, 1999, **1**, 1745–1747; (*h*) G. J. Dawson, J. M. J. Williams and S. J. Coote, *Tetrahedron: Asymmetry*, 1995, **6**, 2535–2546.

25 (*a*) M. A. Jalil, S. Fujinami, H. Sendai and H. Nishikawa, *J. Chem. Soc., Dalton Trans.*, 1999, 1655–1662; (*b*) M. A. Jalil, S. Fujinami and H. Nishikawa, *J. Chem. Soc., Dalton Trans.*, 1999, 3499–3505.

26 (*a*) C. A. Busacca, D. Grossbach, R. C. So, E. M. O'Brien and E. M. Spinelli, *Org. Lett.*, 2003, **5**, 595–598; (*b*) F. Menges, M. Neuburger and A. Pfaltz, *Org. Lett.*, 2002, **4**, 4713–4716.

27 (*a*) D. B. Grotjahn, D. Combs, S. Van, G. Aguirre and F. Ortega, *Inorg. Chem.*, 2000, **39**, 2080–2086; (*b*) G. Esquius, J. Pons, R. Yáñez, J. Ros, R. Mathieu, B. Donnadieu and N. Lugan, *Eur. J. Inorg. Chem.*, 2002, 2999–3006; (*c*) G. Esquius, J. Pons, R. Yáñez, J. Ros, R. Mathieu, N. Lugan and B. Donnadieu, *J. Organomet. Chem.*, 2003, **667**, 126–134; (*d*) T. G. Schenck, J. M. Downes, C. R. C. Milne, P. B. Mackenzie, T. G. Boucher, J. Whelan and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2334–2337.

28 (*a*) H. Yang, M. Alvarez, N. Lugan and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1995, 1721–1722; (*b*) H. Yang, A. A.-Gressier, N. Lugan and R. Mathieu, *Organometallics*, 1997, **16**, 1401–1409.

29 During the course of our studies an analogous ligand to PyP, $Me_2$PyP (1-(2-diphenylphosphino)ethyl-3,5-dimethylpyrazole) and its complexes with Rh(I), Ru(II) were reported[27b,c].

30 P. López, C. G. Seipelt, P. Merkling, L. Sturz, J. Álvarez, A. Dölle, M. D. Zeidler, S. Cerdán and P. Ballesteros, *Bioorg. Med. Chem.*, 1999, **7**, 517–527.

31 C. K. Johnson, ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

32 S. R. Hall, D. J. du Boulay, and R. Olthof-Hazekamp, (Editors), Xtal3.6 System, University of Western Australia, 1999.

33 D. F. Rendle, A. Storr and J. Trotter, *Can. J. Chem.*, 1975, **53**, 2944–2954.

34 P. Schnider, G. Koch, R. Prétôt, G. Wang, F. M. Bohnen, C. Krüger and A. Pfaltz, *Chem. Eur. J.*, 1997, **3**, 887–892.

35 R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339–2343.

36 D. Roberto, E. Cariati, R. Psaro and R. Ugo, *Organometallics*, 1994, **13**, 4227–4231.

37 U. Klabunde, *Inorg. Synth.*, 1974, **15**, 82–84.

38 D. M. Roundhill, R. A. Bechtold and S. G. N. Roundhill, *Inorg. Chem.*, 1980, **19**, 284–289.

39 (*a*) D. Masui, T. Kochi, Z. Tang, Y. Ishii, Y. Mizobe and M. Hidai, *J. Organomet. Chem.*, 2001, **620**, 69–79; (*b*) J. H. Teles, S. Brode and M. Chabanas, *Angew. Chem., Int. Ed.*, 1998, **37**, 1415–1418; (*c*) Y. Kataoka, O. Matsumoto and K. Tani, *Organometallics*, 1996, **15**, 5246–5249; (*d*) T. Murata, Y. Mizobe, H. Gao, Y. Ishii, T. Wakabayashi, F. Nakano, T. Tanase, S. Yano, M. Hidai, I. Echizen, H. Nanikawa and S. Motomura, *J. Am. Chem. Soc.*, 1994, **116**, 3389–3398; (*e*) A. Avshu, R. D. O'Sullivan, A. W. Parkins, N. W. Alcock and R. M. Countryman, *J. Chem. Soc., Dalton Trans.*, 1983, 1619–1624.

40 R. Uma, C. Crévisy and R. Grée, *Chem. Rev.*, 2003, **103**, 27–51.
41 D. F. Shriver and M. A. Dresdzon, *The Manipulation of Air sensitive Compounds*, John Wiley & Sons, New York, 2nd edn., 1986.
42 D. D. Perrin, and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 2nd edn., 1993.
43 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth.*, 1974, **14**, 18–20.
44 G. Giordano and R. H. Crabtree, *Inorg, Synth.*, 1990, **28**, 88–90.
45 J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, 1990, **28**, 84–86.
46 V. D. Bianco and S. Doronzo, *Inorg. Synth.*, 1976, **16**, 161–163.
47 I. Almena, E. Díez-Barra, A. de la Hoz, J. Ruiz, A. Sánchez-Migallón and J. Elguero, *J. Heterocycl. Chem.*, 1998, **35**, 1263–1268.
48 Bruker, SMART, SAINT and XPREP. Area detector control and data integration and reduction software, Bruker Analytical X-ray Instruments Inc., Madison, WI, USA, 1995.
49 Molecular Structure Corporation, teXsan for Windows: Single Crystal Structure Analysis Software, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1997–1998.
50 L. J. Farrugia and WinGX, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
51 P. Coppens, L. Leiserowitz and D. Rabinovich, *Acta Crystallogr.*, 1965, **18**, 1035–1038.
52 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115–119.
53 G. M. Sheldrick, SHELX97 Programs for Crystal Structure Analysis, University of Göttingen. Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
54 (*a*) H. D. Flack, *Acta Crystallogr., Sect A*, 1983, **39**, 876–881; (*b*) G. Bernardinelli and H. D. Flack, *Acta Crystallogr., Sect A*, 1985, **41**, 500–511; (*c*) H. D. Flack and G. Bernardinelli, *Acta Crystallogr., Sect. A*, 1999, **55**, 908–915; (*d*) H. D. Flack and G. Bernardinelli, *J. Appl. Crystallogr.*, 2000, **33**, 1143–1148.