

Thiobenzamidato and thiobenzoato complexes of ruthenium, osmium and iridium*

Stephen D. Robinson,^a Arvind Sahajpal^a and Derek A. Tocher^b

^a Department of Chemistry, Kings College London, Strand, London WC2R 2LS, UK

^b Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

Thiobenzamide reacted with the complexes $[\text{MCl}_2(\text{PPh}_3)_3]$, $[\text{MH}(\text{X})(\text{CO})(\text{PPh}_3)_3]$ ($\text{M} = \text{Ru}$ or Os , $\text{X} = \text{H}$ or Cl) and *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$ in boiling toluene to afford the products $[\text{M}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$, $[\text{MX}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$ and $[\text{IrH}_2\{\text{S}(\text{NH})\text{CPh}\}(\text{PPh}_3)_2]$ respectively. The crystal structure of $[\text{Os}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$ confirms the expected bis(*N,S*-chelate) formulation and has established the presence of *cis*-phosphorus, *cis*-nitrogen and *trans*-sulfur donor atom pairs within a highly distorted octahedral co-ordination sphere. Thiobenzoic acid reacted with $[\text{MCl}_2(\text{PPh}_3)_3]$ and $[\text{MH}(\text{X})(\text{CO})(\text{PPh}_3)_3]$ under similar conditions to yield $[\text{M}\{\text{S}(\text{O})\text{CPh}\}_2(\text{PPh}_3)_2]$ and $[\text{M}\{\text{S}(\text{O})\text{CPh}\}_2(\text{CO})(\text{PPh}_3)_2]$ respectively. The reactions of thiobenzoic acid with *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$ under conditions of increasing severity give $[\text{IrH}_2\{\text{S}(\text{O})\text{CPh}\}(\text{PPh}_3)_3]$, $[\text{IrH}\{\text{S}(\text{O})\text{CPh}\}_2(\text{PPh}_3)_2]$ and $[\text{Ir}\{\text{S}(\text{O})\text{CPh}\}_3(\text{PPh}_3)_2]$ the last two of which on carbonylation afford $[\text{IrH}\{\text{S}(\text{O})\text{CPh}\}_2(\text{CO})(\text{PPh}_3)_2]$ and $[\text{Ir}\{\text{S}(\text{O})\text{CPh}\}_3(\text{CO})(\text{PPh}_3)_2]$ respectively. The crystal structure of $[\text{IrH}\{\text{S}(\text{O})\text{CPh}\}_2(\text{PPh}_3)_2]$ has established the presence of *trans* phosphorus and *trans* sulfur donor atom pairs, with the η^1 - and η^2 -thiobenzoate ligands sharing a meridional set of three co-ordination sites. However, the NMR spectra of this complex show two high-field ^1H triplets and two ^{31}P - $\{^1\text{H}\}$ singlets. Possible explanations for this anomalous NMR behaviour, which is also found for the corresponding thioacetate, are advanced.

In the course of work on heteroallylic complexes of the platinum metals we have recently observed reactions between certain ruthenium triphenylphosphine complexes and organic amides $\text{RC}(\text{O})\text{NH}_2$ ($\text{R} = \text{Ph}$, CF_3 , C_2F_5 or C_6F_5) leading to formation of binuclear amidato-bridged products.^{1,2} This behaviour contrasts sharply with that observed for amidines³ and carboxylic acids^{4,5} which react with the same ruthenium precursors to generate more conventional mononuclear products containing chelating heteroallyl ligands. In order further to examine the possibility of a link between the asymmetric nature of the amidate ligands and their tendency to adopt a bridging mode of bonding we have now investigated the reactions of the asymmetric heteroallyls, thiobenzamide and thiobenzoic acid, with a similar series of platinum metal precursors. Unfortunately the products obtained during the course of this study are all mononuclear and therefore lend no support to the hypothesis that in our systems asymmetric heteroallyl ligands have a greater tendency to adopt bridging co-ordination modes than do their symmetric analogues. However the study did afford an iridium(III) derivative $[\text{IrH}\{\text{S}(\text{O})\text{CPh}\}_2(\text{PPh}_3)_2]$ which shows NMR evidence compatible with the presence of a temperature-dependent mixture of two isomeric or solvated forms.

Experimental

Thiobenzamide, thiobenzoic acid and thioacetic acid were obtained from the Aldrich Chemical Co. and used as supplied. Other reagents, experimental techniques and instrumentation were as described in the preceding paper in this series.¹ Spectroscopic data are given in Table 1.

Preparations

All products described were isolated and purified by a standard procedure. The crude reaction solutions, after cooling to ambient temperature, were filtered and then concentrated under

reduced pressure to leave oils. These were crystallised from CH_2Cl_2 -MeOH to afford the pure crystalline materials.

$[\text{Ru}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$. Dichlorotris(triphenylphosphine)ruthenium (0.6 g, 0.62 mmol) and thiobenzamide (0.34 g, 2.48 mmol) were heated under reflux in toluene (40 cm³) for ca. 6 h to give a dark red-brown solution. Standard work-up gave dark orange-brown crystals (0.31 g, 63%), m.p. 170–172 °C (Found: C, 64.0; H, 4.95; N, 2.9; S, 7.25. Calc. for $\text{C}_{50}\text{H}_{42}\text{N}_2\text{P}_2\text{RuS} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 64.5; H, 4.6; N, 3.0; S, 6.8%).

$[\text{RuH}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$. Carbonyldihydridotris(triphenylphosphine)ruthenium (0.8 g, 0.87 mmol) and thiobenzamide (0.48 g, 3.5 mmol) were heated under reflux in toluene (40 cm³) for ca. 30 min to give a dark red solution. Standard work-up gave light brown microcrystals (0.4 g, 59%), decomp. 175–177 °C (Found: C, 64.35; H, 4.95; N, 1.7. Calc. for $\text{C}_{44}\text{H}_{37}\text{NOP}_2\text{RuS} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 64.2; H, 4.6; N, 1.7%).

$[\text{RuCl}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$. Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.6 g, 0.63 mmol) and thiobenzamide (0.32 g, 2.3 mmol) were heated under reflux in toluene (40 cm³) for ca. 6 h to give a dark red-brown solution. Standard work-up gave orange microcrystals (0.28 g, 55%), decomp. 208–210 °C (Found: C, 62.15; H, 4.3; N, 1.45. Calc. for $\text{C}_{44}\text{H}_{36}\text{ClNOP}_2\text{RuS} \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 61.6; H, 4.3; N, 1.6%).

$[\text{Os}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$. Dichlorotris(triphenylphosphine)osmium (0.5 g, 0.49 mmol) and thiobenzamide (0.28 g, 2.04 mmol) were heated under reflux in degassed toluene (40 cm³) for ca. 5 h to give a dark red-brown solution. Standard work-up gave dark maroon crystals (0.26 g, 54%), m.p. 174–176 °C (Found: C, 59.85; H, 4.05; N, 2.65. Calc. for $\text{C}_{50}\text{H}_{42}\text{N}_2\text{OsP}_2\text{S}_2$: C, 60.85; H, 4.3; N, 2.85%).

$[\text{OsH}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$. Carbonyldihydridotris(triphenylphosphine)osmium (0.4 g, 0.38 mmol) and thiobenzamide (0.23 g, 1.56 mmol) were heated under reflux in toluene (40 cm³) for ca. 6 h to give a dark red-brown solution.

* Complexes of the platinum metals. Part 48.¹

Standard work-up gave yellow microcrystals (0.19 g, 58%), decomp. 178–180 °C (Found: C, 58.75; H, 4.4; N, 1.45. Calc. for $C_{44}H_{37}NOOsP_2S \cdot 0.5CH_2Cl_2$: C, 58.0; H, 4.2; N, 1.5%).

[Os{S(NH)CPh}(CO)(PPh₃)₂] $\cdot 0.5CH_2Cl_2$. Carbonylchlorohydridotris(triphenylphosphine)osmium (0.6 g, 0.58 mmol) and thiobenzamide (0.32 g, 2.33 mmol) were heated under reflux in toluene (40 cm³) for ca. 15 h to give a dark red-brown solution. Standard work-up gave orange microcrystals (0.27 g, 52%), m.p. 225–227 °C (Found: C, 56.95; H, 3.75; N, 1.05. Calc. for $C_{44}H_{36}ClNOOsPS \cdot 0.5CH_2Cl_2$: C, 55.85; H, 3.9; N, 1.45%).

[IrH₂{S(NH)CPh}(PPh₃)₂]. *mer*-Trihydridotris(triphenylphosphine)iridium (0.4 g, 0.51 mmol) and thiobenzamide (0.1 g, 0.72 mmol) were heated under reflux in toluene (40 cm³) for ca. 75 min to give a yellow solution. Standard work-up gave very pale yellow microcrystals (0.21 g, 61.4%), m.p. 198–200 °C (Found: C, 60.15; H, 4.5; N, 1.85. Calc. for $C_{43}H_{38}IrNP_2S$: C, 60.4; H, 4.5; N, 1.65%).

[Ru{S(O)CPh}₂(PPh₃)₂]. Dichlorotris(triphenylphosphine)ruthenium (0.8 g, 0.84 mmol) and thiobenzoic acid (0.5 g, 3.62 mmol) were heated under reflux in toluene (40 cm³) for ca. 4.5 h to give a dark red-brown solution. Standard work-up gave orange microcrystals (0.65 g, 87%), m.p. 196–198 °C (Found: C, 65.95; H, 4.6. Calc. for $C_{50}H_{40}O_2P_2RuS_2$: C, 66.7; H, 4.5%).

[Ru{S(O)CPh}₂(CO)(PPh₃)₂]. *Method A.* Carbonyldihydridotris(triphenylphosphine)ruthenium (0.8 g, 0.87 mmol) and thiobenzoic acid (0.5 g, 3.62 mmol) were heated under reflux in toluene (40 cm³) for ca. 90 min to give an orange-red solution. Standard work-up gave orange microcrystals (0.75 g, 93%), m.p. 242–245 °C (Found: C, 65.5; H, 4.6. Calc. for $C_{51}H_{40}O_3P_2RuS_2$: C, 66.0; H, 4.35%).

Method B. Carbonylchlorohydridotris(triphenylphosphine)ruthenium (0.6 g, 0.63 mmol) and thiobenzoic acid (0.35 g, 2.53 mmol) were heated in boiling toluene (40 cm³) for ca. 5 h to give an orange solution. Standard work-up gave orange microcrystals (0.55 g, 95%) identical to those obtained by method A (Found: C, 65.65; H, 4.15. Calc. for $C_{51}H_{40}O_3P_2RuS_2$: C, 66.0; H, 4.35%).

[Os{S(O)CPh}₂(PPh₃)₂]. Dichlorotris(triphenylphosphine)osmium (0.5 g, 0.49 mmol) and thiobenzoic acid (0.28 g, 2.0 mmol) were heated under reflux in degassed toluene (40 cm³) for ca. 4.5 h to give a dark red-brown solution. After evaporation to dryness under reduced pressure the residue was dissolved in dichloromethane and the solution diluted with methanol whereupon a small amount of impure material deposited. This was filtered off and the filtrate set aside to crystallise. After 2 d the major product had deposited as dark brown microcrystals (0.28 g, 57%), m.p. 135–137 °C (Found: C, 62.2; H, 3.85. Calc. for $C_{50}H_{40}O_2OsP_2S_2$: C, 60.7; H, 4.1%).

[Os{S(O)CPh}₂(CO)(PPh₃)₂]. *Method A.* Carbonyldihydridotris(triphenylphosphine)osmium (0.25 g, 0.25 mmol) and thiobenzoic acid (0.15 g, 1.08 mmol) were heated under reflux in toluene (40 cm³) for ca. 18 h to give a dark red-brown solution. Standard work-up gave brown microcrystals (0.18 g, 72%) identical to an authentic specimen prepared by method B.

Method B. As for method A, but using carbonylchlorohydridotris(triphenylphosphine)osmium in place of carbonyldihydridotris(triphenylphosphine)osmium. Product isolated as chocolate brown crystals (92%), m.p. 257–259 °C (Found: C, 59.9; H, 4.15. Calc. for $C_{51}H_{40}O_3OsP_2S_2$: C, 60.2; H, 3.95%).

[IrH₂{S(O)CPh}(PPh₃)₃] $\cdot 0.5CH_2Cl_2$. *mer*-Trihydridotris(triphenylphosphine)iridium (0.4 g, 0.5 mmol) and thiobenzoic acid (0.07 g, 0.51 mmol) were heated under reflux in benzene (40 cm³) for ca. 30 min to afford a pale yellow solution. Stand-

ard work-up gave white microcrystals (0.26 g, 46%), m.p. 203–205 °C (Found: C, 63.45; H, 4.45. Calc. for $C_{61}H_{52}IrOP_3S \cdot 0.5CH_2Cl_2$: C, 63.65; H, 4.6%).

[IrH{S(O)CPh}₂(PPh₃)₂]. *mer*-Trihydridotris(triphenylphosphine)iridium (0.35 g, 0.44 mmol) and thiobenzoic acid (0.124 g, 0.90 mmol) were heated under reflux in toluene (40 cm³) for ca. 40 min to give a yellow solution. Standard work-up gave yellow microcrystals (0.3 g, 69%), m.p. 235–236 °C (Found: C, 60.35; H, 4.05. Calc. for $C_{50}H_{41}IrO_2P_2S_2$: C, 60.5; H, 4.15%).

[IrH{S(O)CMe}(PPh₃)₂]. *mer*-Trihydridotris(triphenylphosphine)iridium (0.4 g, 0.51 mmol) and thioacetic acid (0.1 g, 1.31 mmol) were heated under reflux in toluene (40 cm³) for ca. 40 min to give a yellow solution. Standard work-up gave pale yellow microcrystals (0.26 g, 59%), m.p. 197–199 °C (Found: C, 55.0; H, 4.2. Calc. for $C_{40}H_{37}IrO_2P_2S_2$: C, 55.3; H, 4.3%).

[Ir{S(O)CPh}₃(PPh₃)₂]. Hydridobis(thiobenzoato)bis(triphenylphosphine)iridium (0.35 g, 0.35 mmol) and thiobenzoic acid (0.15 g, 1.09 mmol) were heated under reflux in toluene (30 cm³) for ca. 2 h to give an orange-yellow solution. Standard work-up gave yellow-orange microcrystals (0.2 g, 51%), decomp. 272–274 °C (Found: C, 60.5; H, 4.1. Calc. for $C_{57}H_{45}IrO_3P_2S_3$: C, 60.65; H, 4.0%).

[IrH{S(O)CPh}₂(CO)(PPh₃)₂] $\cdot 0.5CH_2Cl_2$. Hydridobis(thiobenzoato)bis(triphenylphosphine)iridium (0.15, 0.14 mmol) was dissolved in toluene (30 cm³) and heated under reflux for ca. 20 min with slow passage of carbon monoxide. Standard work-up of the yellow solution gave very pale yellow microcrystals (0.12 g, 84%), m.p. 222–224 °C (Found: C, 58.2; H, 3.85. Calc. for $C_{51}H_{41}IrO_3P_2S_2 \cdot 0.5CH_2Cl_2$: C, 58.2; H, 3.95%).

[Ir{S(O)CPh}₃(CO)(PPh₃)₂] $\cdot 0.5CH_2Cl_2$. Tris(thiobenzoato)bis(triphenylphosphine)iridium (0.08 g, 0.071 mmol) in toluene (25 cm³) was heated under reflux for ca. 1 h with slow passage of carbon monoxide. The solution was then cooled and evaporated under reduced pressure to yield an oil which on crystallisation from CH_2Cl_2 –MeOH afforded orange microcrystals (0.07 g, 87%), m.p. 246–248 °C (Found: C, 58.2; H, 3.75. Calc. for $C_{58}H_{45}IrO_4P_2S_3 \cdot 0.5CH_2Cl_2$: C, 58.6; H, 3.85%).

Crystallography

A red single crystal of $[Os\{S(NH)CPh\}_2(PPh_3)_2]$ of approximate size 0.60 × 0.20 × 0.06 mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample at 293 K using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-K α radiation ($\lambda = 0.71073$ Å).

The lattice vectors were identified by the application of the automatic indexing routine of the diffractometer to the positions of 38 reflections taken from a rotation photograph and centred by the diffractometer. The ω – 2θ technique was used to measure 7887 reflections (7458 unique) in the range $5 < 2\theta < 50^\circ$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz and polarisation effects, and empirically for absorption. The 6536 unique data with $I \geq 2.0\sigma(I)$ were used to solve and refine the structure in the triclinic space group *P*1.

Crystal data. $C_{50}H_{42}N_2OsP_2S_2$, *M* = 987.12, triclinic, space group *P*1, *a* = 10.746(2), *b* = 11.077(2), *c* = 18.152(4) Å, α = 88.29(3), β = 85.79(3), γ = 81.53(3)°, *U* = 2131 Å³, *Z* = 2, *D*_c = 1.54 g cm^{−3}, *F*(000) = 988, μ (Mo-K α) = 32.03 cm^{−1}.

The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while the hydrogens were placed in

idealised positions (C–H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08 \text{ Å}^2$). The final cycle of least-squares refinement included 514 parameters for 6536 variables and did not shift any parameter by more than 0.001 times its standard deviation. The final R , R' values were 0.0334 and 0.0800 [weighting scheme $w^{-1} = \sigma^2 F_o^2 + (0.0452P)^2 + 3.91P$] and the final Fourier-difference synthesis was featureless with no peaks greater than 0.80 e Å^{-3} .

The structure solution used the SHELXL 93⁶ program package on a micro Vax II computer. The molecular structure is shown in Fig. 1, selected bond lengths and angles in Table 2.

A yellow single crystal of $[\text{IrH}\{\text{S}(\text{O})\text{CPh}\}_2(\text{PPh}_3)_2]$ of approximate size $0.40 \times 0.35 \times 0.35 \text{ mm}$ was mounted on a glass fibre. Data were collected as above.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 34 reflections taken from a rotation photograph and centred by the diffractometer. The ω – 2θ technique was used to measure 7990 reflections (7609 unique) in the range $5 \leq 2\theta \leq 50^\circ$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected as above. The 6480 unique data with $I \geq 3.0\sigma(I)$ were used to solve and refine the structure in the triclinic space group $P\bar{1}$.

Crystal data. $\text{C}_{50}\text{H}_{41}\text{IrO}_2\text{P}_2\text{S}_2$, $M = 992.161$, triclinic, space group $P\bar{1}$, $a = 12.353(3)$, $b = 13.661(3)$, $c = 14.497(3) \text{ Å}$, $\alpha = 87.55(2)$, $\beta = 68.89(2)$, $\gamma = 72.04(2)^\circ$, $U = 2165 \text{ Å}^3$, $Z = 2$, $D_c = 1.52 \text{ g cm}^{-3}$, $F(000) 992$, $\mu(\text{Mo-K}\alpha) 32.7 \text{ cm}^{-1}$.

The structure was solved, developed and refined as above. The hydridic ligand was not located and was omitted from the refinement. Nevertheless its position is readily apparent in the fully refined structure. The final cycle of least-squares refinement (based on F^2) included 514 parameters for 6480 variables and did not shift any parameter by more than 0.001 times its standard deviation. The final R , R' values were 0.0305 and 0.0348 [weighting scheme $w^{-1} = \sigma^2(F) + 0.00154F^2$] and the final Fourier-difference map was featureless with no peaks greater than 0.80 e Å^{-3} .

The structure solution was as above. The molecular structure is shown in Fig. 2, selected bond lengths and angles in Table 3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/360.

Results and Discussion

Thiobenzamidato complexes

The reactions of thiobenzamide with various ruthenium precursors afford simple mononuclear derivatives; there is no evidence of the formation of binuclear species analogous to those previously obtained with benzamide.² Thus with $[\text{RuCl}_2(\text{PPh}_3)_3]$ in boiling toluene thiobenzamide forms the mononuclear bis(chelate) complex $[\text{Ru}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$ in good yield as air-stable orange-brown crystals. There are five possible geometric isomers for a bis(chelate) complex of this form and the rather sparse spectroscopic evidence available does not permit an unambiguous stereochemical assignment. However, by analogy with the osmium analogue which has been characterised by X-ray diffraction methods (see below), we propose a *cis*- PPh_3 , *cis*-N, *trans*-S stereochemical arrangement similar to that previously reported for $[\text{Ru}(\text{C}_5\text{H}_4\text{NS-2})_2(\text{PPh}_3)_2]$.⁷

The reaction of $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ with thiobenzamide gives rise to a mononuclear species $[\text{RuH}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$. Again we have a sharp contrast between this product and the binuclear cyclometallated complex $[(\text{Ph}_3\text{P})(\text{OC})-$

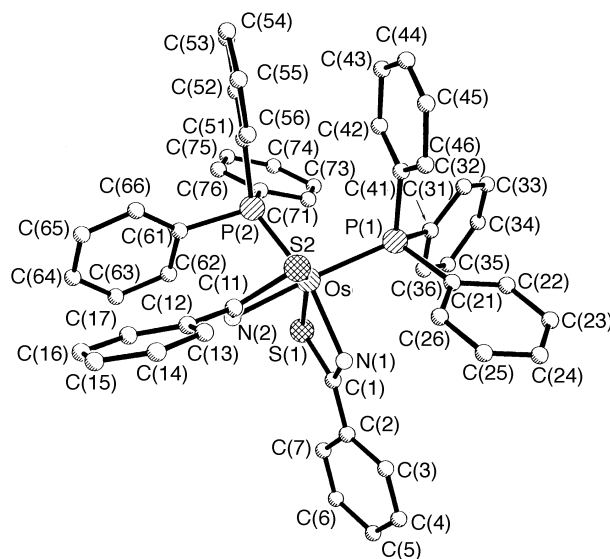


Fig. 1 Molecular structure of $[\text{Os}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$

$\text{Ru}\{\mu\text{-NH}(\text{O})\text{CC}_6\text{H}_4\}\{\mu\text{-NH}(\text{O})\text{CPh}\}(\mu\text{-H})\text{Ru}(\text{CO})(\text{PPh}_3)_2]$ obtained from the parallel reaction with benzamide.² The NMR spectra for $[\text{RuH}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$ reveal the presence of two geometrical isomers. For each a ^{31}P - $\{^1\text{H}\}$ singlet and a high-field ^1H triplet [$^2J_{\text{HP}(\text{cis})}$ ca. 20 Hz] are consistent with *trans* phosphines stereochemistry. However, the presence of an additional coupling [$^3J_{\text{HH}} = 2.6 \text{ Hz}$] in the high-field ^1H NMR spectrum of the major isomer allows it to be positively identified as the one with hydride *trans* to the NH group of the thiobenzamide. It follows that the minor isomer (ca. 10%) has the hydride ligand *trans* to sulfur.

The reaction of $[\text{RuH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$ with thiobenzamide affords an air-stable orange crystalline product of stoichiometry $[\text{RuCl}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$. The ^{31}P - $\{^1\text{H}\}$ NMR spectrum again reveals the presence of two isomers each giving rise to a singlet, indicative of *trans* phosphines. Structures with the chloride ligand *trans* to the N- and S-donor atoms respectively of the thiobenzamidate ligand can be assumed. However there is no evidence to indicate which is the major isomer.

The reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ with thiobenzamide in boiling toluene affords the osmium bis(chelate) complex $[\text{Os}\{\text{S}(\text{NH})\text{CPh}\}_2(\text{PPh}_3)_2]$ as dark maroon air-stable crystals. As was the case with the ruthenium analogue there are insufficient spectroscopic data to permit a stereochemical assignment. Therefore a crystal structure determination was undertaken. The molecular structure is shown in Fig. 1, selected bond length and angle data in Table 2. The molecule has a highly distorted octahedral geometry reflecting the small bite angles, S–Os–N $65.77(12)$ and $65.57(12)^\circ$, of the thioamidate ligands. The bulky triphenylphosphine ligands are mutually *cis* as are the N-donor atoms of the thioamidate ligands. The two S-donor atoms are essentially *trans* to each other with S–Os–S $152.72(5)^\circ$. The bond lengths are typical for octahedral osmium(II).

Thiobenzamide reacts with the osmium complex $[\text{OsH}_2(\text{CO})(\text{PPh}_3)_3]$ to give $[\text{OsH}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$ which, in contrast to its ruthenium analogue, is obtained in an isomerically pure state. The NMR spectra comprising a ^{31}P - $\{^1\text{H}\}$ singlet and a high-field ^1H triplet with additional coupling to the thiobenzamidato NH group ($^3J_{\text{HH}} = 2.0 \text{ Hz}$) clearly establish a *trans*-phosphines stereochemistry with hydride *trans* to the N-donor atom of the thiobenzamidate ligand. A similar reaction with the osmium complex $[\text{OsH}(\text{Cl})(\text{CO})(\text{PPh}_3)_3]$ afforded a mixture of the two *trans*-phosphines isomers of $[\text{OsCl}\{\text{S}(\text{NH})\text{CPh}\}(\text{CO})(\text{PPh}_3)_2]$.

In contrast to benzamide which reacts with *mer*- $[\text{IrH}_3(\text{PPh}_3)_3]$ to form a monodentate N-bonded derivative $[\text{IrH}_2\{\text{NH}(\text{O})-$

Table 1 Spectroscopic data

Complex	IR ^a /cm ⁻¹		NMR (δ , J/Hz) ^b	
	$\nu(\text{MH})$	$\nu(\text{CO})$	¹ H	³¹ P-{H}
(a) Thiobenzamide derivatives [L = NH(S)CPh]				
[RuL ₂ (PPh ₃) ₂]	—	—	—	37.66 (br)
[RuH(L)(CO)(PPh ₃) ₂] ^c	Broad unresolved ca. 1900	—	−12.29 (t of d, ² J _{HP} 20.5; ³ J _{HH} 2.6) −2.58 (t, ² J _{HP} 10.5)	50.96 (s) 46.11 (s)*
[RuCl(L)(CO)(PPh ₃) ₂] ^c	Broad unresolved ca. 1850	—	—	33.68 (s) 41.22 (s)*
[OsL ₂ (PPh ₃) ₂]	—	—	—	−0.5 (s)
[OsH(L)(CO)(PPh ₃) ₂]	2050	1875	−14.04 (t of d, ² J _{HP} 17.8; ³ J _{HH} 2.0)	22.21 (s)
[OsCl(L)(CO)(PPh ₃) ₂] ^c	—	1885 1925	—	11.77 (s) −2.95 (s)*
[IrH ₂ L(PPh ₃) ₂]	2105 2185	—	−21.22 (t of d, ² J _{HP} 16.0; ² J _{HH} 6.5) −21.04 (t of d of d, ² J _{HP} 17.7; ² J _{HH} 6.5; ³ J _{HH} 3.7)	21.02 (s)
(b) Thiobenzoate and thioacetate derivatives [L = O(S)CPh, L' = O(S)CMe]				
[RuL ₂ (PPh ₃) ₂]	—	—	—	60.46 (s)
[RuL ₂ (CO)(PPh ₃) ₂]	—	1945	—	43.55 (s)
[OsL ₂ (PPh ₃) ₂]	—	—	—	44.0 (s)
[OsL ₂ (CO)(PPh ₃) ₂]	—	1930	—	17.74 (s)
[IrH ₂ L(PPh ₃) ₃]	2085 2185	—	−11.08 (d of t of d, ² J _{HP} 128 and 19.5; ² J _{HH} 4.7) −15.08 (d of t of d, ² J _{HP} 10.4 and 19.5; ² J _{HH} 4.7)	6.88 (d, ² J _{PP} 11.4) 1.52 (t, ² J _{PP} 11.4)
[IrHL ₂ (PPh ₃) ₂] ^d	—	—	−25.3 (t, ² J _{HP} 13) −29.38 (t, ² J _{HP} 13)	9.06 (s) 253 K 18.33 (s)
	2220	—	−25.6 (br) −29.2 (br) −29.3 (br)	8.33 (s) 293 K 17.82 (s)
			−29.33 (t, ² J _{HP} 14)	16.92 (s) 353 K
[IrHL' ₂ (PPh ₃) ₂] ^d	2240	—	−25.71 (t, ² J _{HP} 13.4) −29.83 (t, ² J _{HP} ≈ 13)	373 K 9.85 (s) 256 K
			−26.0 (br) −29.9 (br) −29.95 (s)	18.80 (s) 8.67 (br) 296 K 18.22 (br)
				16.79 (s) 380 K
[IrL ₃ (PPh ₃) ₂]	—	—	—	4.08 (s)
[IrHL ₂ (CO)(PPh ₃) ₂]	2140	2030	−11.15 (t, ² J _{HP} 12.5)	3.37 (s)
[IrL ₃ (CO)(PPh ₃) ₂]	—	2030	—	−13.05 (s)

^a Nujol mulls. ^b Spectra run in CDCl₃ solution at 298 K unless otherwise specified. ^c Isomer mixtures (data for minor isomer indicated by asterisk).

^d Variable-temperature NMR data recorded in toluene solution.

CPh}(PPh₃)₃],² thiobenzamide affords an N,S-chelate product [IrH₂{S(NH)CPh}(PPh₃)₂] which can be isolated in good yield as pale yellow crystals. This difference in behaviour no doubt reflects the greater affinity of iridium(III) for S- as opposed to O-donor ligands. The expected *trans*-phosphine stereochemistry is confirmed for [IrH₂{S(NH)CPh}(PPh₃)₂] by the NMR data, and the presence of an additional coupling (³J_{HH} = 3.7 Hz) allows the high-field ¹H signal at δ −21.04 to be attributed to the hydride ligand *trans* to the NH group.

Thiobenzoato (and thioacetato) complexes

The monothiocarboxylato complexes obtained are also mononuclear and, in several instances, are identical with or similar to products previously reported by other groups.^{4,5,8,9} Discussion is therefore kept to a minimum. However one pair of iridium(III) complexes [IrH{S(O)CR}₂(PPh₃)₂] (R = Me or Ph) display anomalous NMR spectra and merit fuller attention.

The reaction of thiobenzoic acid with [RuCl₂(PPh₃)₃] in refluxing toluene affords [Ru{S(O)CPh}₂(PPh₃)₂] as orange air-stable crystals. This complex has previously been prepared from [RuCl₂(PPh₃)₃] and sodium monothioacetate in refluxing acetone, and assigned an all-*trans* structure on the basis of chemical and spectroscopic evidence.⁸ Thiobenzoic acid reacts with [RuH₂(CO)(PPh₃)₃] or with [RuH(Cl)(CO)(PPh₃)₃] in refluxing toluene to afford [Ru{S(O)CPh}₂(CO)(PPh₃)₂] as air-stable orange microcrystals, again there is no evidence for the formation of any binuclear products. The spectroscopic data for [Ru{S(O)CPh}₂(CO)(PPh₃)₂] (see Table 1) are virtually iden-

tical with those previously reported for the corresponding monothioacetate complex.¹⁰ We therefore conclude that the monothioacetate complex has the same *trans*-P *trans*-S ligand stereochemistry as that previously determined for the monothioacetate complex. Presumably the thiobenzoate like the latter complex displays rapid interchange of η^1 - and η^2 -thiocarboxylate groups in solution. However, in the absence of a suitable NMR label it has not been possible to confirm this hypothesis. The reaction of [OsCl₂(PPh₃)₃] with thiobenzoic acid in refluxing toluene affords [Os{S(O)CPh}₂(PPh₃)₂] as dark brown air-stable crystals. The complex [Os{S(O)CPh}₂(CO)(PPh₃)₂] was similarly obtained from [OsH₂(CO)(PPh₃)₃] or [OsH(Cl)(CO)(PPh₃)₃] as air-stable brown crystals, and is tentatively assigned the same stereochemistry as that of its ruthenium analogue.

The reaction of *mer*-[IrH₃(PPh₃)₃] with thiobenzoic acid under increasingly vigorous conditions successively affords three products [IrH₂{S(O)CPh}(PPh₃)₃], [IrH{S(O)CPh}₂(PPh₃)₂] and [Ir{S(O)CPh}₃(PPh₃)₂]. The first of these was reluctant to carbonylate under mild conditions (refluxing benzene) and gave a mixture of products when more vigorous treatment was used. However the other two complexes carbonylated smoothly to yield [IrH{S(O)CPh}₂(CO)(PPh₃)₂] and [Ir{S(O)CPh}₃(CO)(PPh₃)₂] respectively. For four of these products the spectroscopic data are consistent with their formulation as rigid, octahedral iridium(III) species. However complete stereochemical assignment has been possible in only two cases, [IrH₂{S(O)CPh}(PPh₃)₃] which has one hydride *trans* to S-bonded thiobenzoate, and [IrH{S(O)CPh}₂(CO)(PPh₃)₂]

Table 2 Selected bond lengths (Å) and angles (°) for [Os{S(NH)C-Ph}₂(PPh₃)₂]

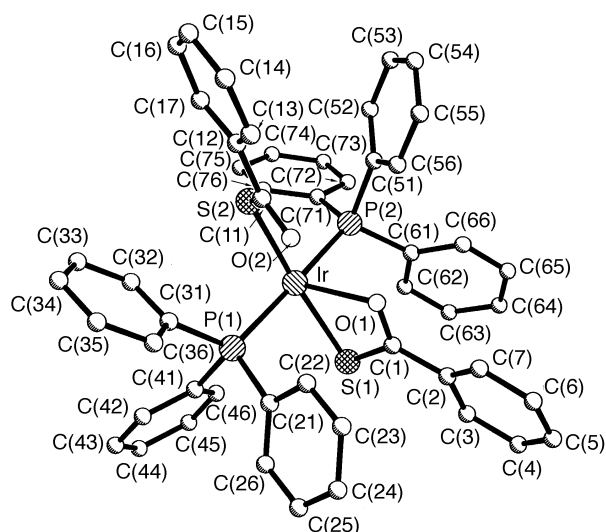
Os–N(2)	2.129(4)	P(1)–C(21)	1.868(6)
Os–N(1)	2.130(4)	P(2)–C(71)	1.840(5)
Os–P(1)	2.298(2)	P(2)–C(51)	1.852(5)
Os–P(2)	2.309(2)	P(21)–C(61)	1.856(5)
Os–S(2)	2.4225(13)	S(1)–C(1)	1.741(5)
Os–S(1)	2.4292(14)	S(2)–C(11)	1.728(5)
P(1)–C(41)	1.827(6)	N(1)–C(1)	1.303(7)
P(1)–C(31)	1.845(5)	N(2)–C(11)	1.297(6)
N(2)–Os–N(1)	85.6(2)	S(2)–Os–S(1)	152.72(5)
N(2)–Os–P(1)	159.45(12)	C(41)–P(1)–Os	113.7(2)
N(1)–Os–P(1)	90.79(12)	C(31)–P(1)–Os	124.3(2)
N(2)–Os–P(2)	87.87(12)	C(21)–P(1)–Os	112.8(2)
N(1)–Os–P(2)	160.23(13)	C(71)–P(2)–Os	117.3(2)
P(1)–Os–P(2)	101.62(5)	C(51)–P(2)–Os	124.7(2)
N(2)–Os–S(2)	65.57(12)	C(61)–P(2)–Os	108.3(2)
N(1)–Os–S(2)	94.70(12)	C(1)–S(1)–Os	81.0(2)
P(1)–Os–S(2)	94.68(5)	C(11)–S(2)–Os	81.2(2)
P(2)–Os–S(2)	99.51(5)	C(1)–N(1)–Os	104.3(3)
N(2)–Os–S(1)	92.91(12)	C(11)–N(2)–Os	104.2(3)
N(1)–Os–S(1)	65.77(12)	N(1)–C(1)–S(1)	108.8(4)
P(1)–Os–S(1)	104.01(5)	N(2)–C(11)–S(2)	109.1(4)
P(2)–Os–S(1)	96.03(5)		

Table 3 Selected bond lengths (Å) and angles (°) for [IrH{η¹-S(O)-CPh}{η²-S(O)CPh}(PPh₃)₂]

Ir–P(1)	2.326(1)	Ir–P(2)	2.342(1)
Ir–S(1)	2.388(1)	Ir–S(2)	2.352(1)
Ir–O(1)	2.303(4)	P(1)–C(21)	1.834(4)
P(1)–C(31)	1.836(4)	P(1)–C(41)	1.846(6)
P(2)–C(51)	1.834(7)	P(2)–C(61)	1.833(4)
P(2)–C(71)	1.843(5)	S(1)–C(1)	1.719(6)
S(2)–C(11)	1.740(6)	O(1)–C(1)	1.251(6)
O(2)–C(11)	1.230(6)	C(1)–C(2)	1.485(6)
C(11)–C(12)	1.488(8)		
P(1)–Ir–P(2)	174.4(1)	P(1)–Ir–S(1)	86.4(1)
P(2)–Ir–S(1)	92.6(1)	P(1)–Ir–S(2)	94.7(1)
P(2)–Ir–S(2)	86.9(1)	S(1)–Ir–S(2)	173.3(1)
P(1)–Ir–O(1)	98.0(1)	P(2)–Ir–O(1)	86.5(1)
S(1)–Ir–O(1)	65.0(1)	S(2)–Ir–O(1)	108.3(1)
Ir–P(1)–C(21)	113.1(2)	Ir–P(1)–C(31)	119.2(2)
Ir–P(2)–C(51)	114.8(2)	Ir–P(1)–C(41)	113.7(2)
Ir–S(1)–C(1)	82.5(2)	Ir–P(2)–C(61)	115.0(2)
Ir–O(1)–C(1)	97.1(3)	Ir–P(2)–C(71)	115.7(2)
S(1)–C(1)–C(2)	122.5(4)	Ir–S(2)–C(11)	106.4(2)
S(2)–C(11)–O(2)	123.3(5)	S(1)–C(1)–O(1)	115.4(3)
O(2)–C(11)–C(12)	119.4(5)	O(1)–C(1)–C(2)	122.1(5)
		S(2)–C(11)–C(12)	117.3(4)

which has *trans* phosphine and *trans* S-bonded thiobenzoate ligands.

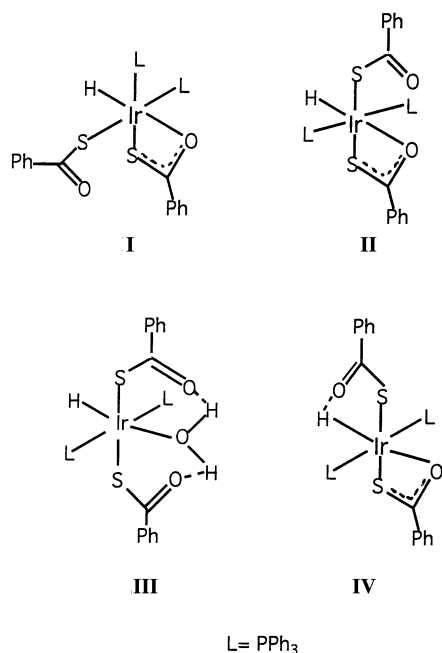
The fifth iridium thiobenzoate complex, [IrH{S(O)CPh}₂(PPh₃)₂], did not conform to expectations. At ambient temperature the high-field ¹H NMR spectrum showed two slightly broad and featureless peaks at *ca.* δ –25.6 and –29.2 while the ³¹P-{¹H} spectrum contained two singlets at *ca.* δ 8.3 and 17.8. Moreover, the spectra were temperature dependent; on cooling to 253 K the ¹H and ³¹P-{¹H} signals at *ca.* δ –25.6 and 8.3 respectively grow at the expense of those at *ca.* δ –29.2 and 17.8 respectively. At the same time the high-field proton resonances gradually sharpen into well defined triplets (²J_{HP} *ca.* 13 Hz). Conversely as the temperature is raised the ¹H and ³¹P-{¹H} signals at *ca.* δ –29.2 and 17.8 respectively grow at the expense of those at *ca.* δ –25.6 and 8.3 until at 373 K the latter pair have disappeared completely. Again this change is accompanied by sharpening of the remaining high-field signal which becomes a sharp well defined triplet. There is little evidence of coalescence in either the ¹H or ³¹P-{¹H} spectra; throughout the temperature range 253–373 K the chemical shifts of the individual resonances remain essentially constant (variation ±0.7 ppm).

**Fig. 2** Molecular structure of [IrH{η¹-S(O)CPh}{η²-S(O)CPh}-(PPh₃)₂]

This suggests the presence of a substantial kinetic barrier rendering the underlying process slow on the NMR time-scale. Finally the chemical shifts recorded for both of the high-field resonances are consistent with hydride *trans* to an O- rather than an S-donor ligand. Confirmation of our NMR observations was provided by the corresponding monothioacetate complex [IrH{S(O)CMe}₂(PPh₃)₂] which displayed essentially similar temperature-dependent NMR data. As a first step towards elucidating the nature of the complexes [IrH{S(O)CR}₂(PPh₃)₂] (R = Me or Ph) and explaining their NMR spectra an X-ray diffraction study was performed on the monothioacetate. The molecular structure is shown in Fig. 2; selected bond lengths and angles are collated in Table 3. The molecule contains an unexceptional octahedral iridium(III) centre co-ordinated to a *trans* pair of triphenylphosphine ligands, an η¹-thiobenzoate and an η²-thiobenzoate. The angle subtended at the iridium centre by the small 'bite' η²-thiobenzoate ligand is 65.0(1)°. The hydride ligand was not located but its presence is indicated by a 'vacancy' in the co-ordination sphere. The bond lengths and angles are typical of octahedral iridium(III) and the structure offers no immediate explanation of the NMR data. We must therefore seek an answer elsewhere. Four possible options, geometric isomers, solvation, rotamers and hydride–carboxylate hydrogen bonding, appear worthy of consideration.

Geometric isomers involving a temperature-dependent equilibrium of *cis* and *trans* phosphines, structures **I** and **II**, both of which would be expected to display rapid η¹/η² thiocarboxylate interchange, are considered improbable. The second possibility, rotamers arising from restricted rotation of the η¹-thiocarboxylate groups about the Ir–S bonds on **II**, seems unlikely since the related complex [IrH{S(O)CPh}₂(CO)(PPh₃)₂] which has a similar stereochemical arrangement of hydride, thiobenzoate and triphenylphosphine ligands does not display anomalous NMR behaviour. An equilibrium between unsolvated **II** and solvated (aquated?) species **III** appears more feasible. Structures involving intramolecular hydrogen bonding between co-ordinated water and carboxylate are well established.¹¹ However the crystal structure of the complex reveals no solvent molecules co-ordinated or otherwise. Furthermore spectroscopic and crystallographic examination of samples crystallised from wet solvent yielded no evidence of solvation.

The final option involves an equilibrium between the fluxional structure **II** and the hydrogen-bonded form **IV**. According to this scenario the η¹/η² interchange process would maintain structure **II** at higher temperatures. At lower temperatures when the fluxional process was frozen out the hydrogen-bonding



interaction between the hydride ligand and the oxygen atom of the monodentate thiocarboxylate ligand would become the dominant force leading to adoption of the alternative structure **IV**. The hydrogen-bonded structure **IV** has a very feasible geometry with an unstrained five-membered ring. However, from an electronic viewpoint hydrogen bonding is a less attractive proposition. Transition-metal hydrides are known to participate in hydrogen-bonding interactions but these are usually of the form $M-H \cdots H-X$ ($X = N$ or O) and involve the hydride ligand acting as a source rather than an acceptor of electron density.^{12–18} An interaction of the form $M-H \cdots O$ similar to the one postulated here has recently been convincingly demonstrated for $[WH_3(O_2CMe)(dppe)_2]$ ($dppe = Ph_2PCH_2CH_2PPh_2$) by X-ray diffraction methods [$WH \cdots O$ 2.33(6) Å].¹⁹ However, in that instance the hydride involved resonated at much lower field (δ 2.92) indicating much less shielding and hence lower electron density than is the case for the hydride ligands in the complexes $[IrH\{S(O)CR\}_2(PPh_3)_2]$. Finally it is interesting that the shift of ca. 4 ppm to lower field observed for the hydride ligand in going from the high- to the low-temperature form matches a similar shift to lower field observed for the hydrogen-bonded hydride ligand relative to its non-hydrogen-bonded neighbours in $[WH_3(O_2CMe)(dppe)_2]$.

However, if the equilibrium process $II \rightleftharpoons IV$ is operating suppression of the η^1/η^2 thiobenzoate exchange process on crystallisation should cause the molecule to adopt the hydrogen-bonded configuration **IV**, and the crystal structure shows no evidence of this occurring. Indeed the oxygen atom of the η^1 -thiobenzoate ligand is directed away from the hydride ligand. Unless this arrangement can be attributed to crystal-packing factors it must be taken as strong evidence against the hydride-carboxylate hydrogen-bonding explanation. We are therefore reluctantly forced to conclude that, on the basis of currently available evidence, a definitive explanation of the observed NMR phenomenon is not forthcoming.

References

- 1 Part 47, S. D. Robinson, A. Sahajpal and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1995, 3497.
- 2 M. B. Hursthouse, M. A. Mazid, S. D. Robinson and A. Sahajpal, *J. Chem. Soc., Dalton Trans.*, 1993, 2835.
- 3 M. B. Hursthouse, M. A. Mazid, S. D. Robinson and A. Sahajpal, *J. Chem. Soc., Dalton Trans.*, 1994, 3615.
- 4 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 1912.
- 5 A. Dobson, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1975, 370.
- 6 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.
- 7 S. R. Fletcher and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1972, 635.
- 8 R. O. Gould, T. A. Stephenson and M. A. Thomson, *J. Chem. Soc., Dalton Trans.*, 1978, 769.
- 9 J. D. Gilbert and G. Wilkinson, *J. Chem. Soc. A*, 1969, 1749.
- 10 P. B. Critchlow and S. D. Robinson, *Inorg. Chem.*, 1978, **17**, 1902.
- 11 P. M. Boyer, C. P. Roy, J. M. Bielski and J. S. Merola, *Inorg. Chim. Acta*, 1996, **245**, 7 and refs. therein.
- 12 J. C. Lee, E. Peris, A. L. Rheingold and R. H. Crabtree, *J. Am. Chem. Soc.*, 1994, **116**, 11014.
- 13 J. C. Lee, A. L. Rheingold, B. Muller, P. S. Pregosin and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1994, 1021.
- 14 E. Peris, J. C. Lee, J. R. Rambo, O. Eisenstein and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 3485.
- 15 A. J. Lough, S. Park, R. Ramachandran and R. H. Morris, *J. Am. Chem. Soc.*, 1994, **116**, 8356.
- 16 S. J. Park, R. Ramachandran, A. J. Lough and R. H. Morris, *J. Chem. Soc., Chem. Commun.*, 1994, 2201.
- 17 D. Milstein, J. C. Calabrese and I. D. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 6387.
- 18 R. C. Stevens, R. Bau, D. Milstein, O. Blum and T. F. Koetzle, *J. Chem. Soc., Dalton Trans.*, 1990, 1429.
- 19 S. A. Fairhurst, R. A. Henderson, D. L. Hughes, S. K. Ibrahim and C. J. Pickett, *J. Chem. Soc., Chem. Commun.*, 1995, 1569.

Received 14th October 1996; Paper 6/07011F