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Schiff Base Complexes of the Rarer Platinum Metals

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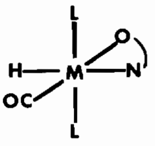
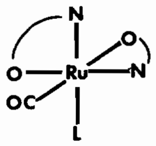
Since their discovery in the mid 19th century, Schiff base complexes of the transition metals have occupied a key position in the development of coordination chemistry [1]. However, their importance in the chemistry of the lighter group VIII metals – iron, cobalt and nickel – is not matched in that of the platinum group metals where Schiff base complexes are few in number. Although recent work [2–5] has gone some way to redress the balance, Schiff base complexes of the platinum group metals remain relatively scarce. We now find that reactions between Schiff bases and hydrido or low oxidation state phosphine complexes of the platinum metals afford convenient routes to a very extensive range of new ruthenium, osmium, rhodium and iridium Schiff base complexes in excellent yield.

Treatment of $RuH_2(CO)(PPh_3)_3$ with bidentate salicylaldimine Schiff bases *o*-$HOC_6H_4CH{=}NR$ (R = Ph, Bz, *o* or *p*-$X{\cdot}C_6H_4$ (X = Me, Cl, Br or NO_2) and *p*-$Me\text{-}C_6H_4CH_2CH_2$) in boiling 2-methoxy ethanol for *ca.* 2 h affords the pale yellow complexes $Ru(OC_6H_4CH{-}NR)H(CO)(PPh_3)_2$. These products are assigned stereochemistry (**I**, M = Ru), on the basis of NMR data (^1H, δ_{RuH} *ca.* −10 ppm (t of d), $^2J(PH)$ *ca.* 21 Hz, $^4J(HH')$ *ca.* 2 Hz; $^{31}P\{^1H\}$, δ_{PPh_3} *ca.* 40–44 ppm (s)). The presence of a measurable coupling $^4J(HH')$ between hydridic and azomethine (–N=CH–) protons clearly favours stereochemistry (**I**) over the alternative arrangement with the hydride *trans* to the O-donor site. More prolonged reactions (10–16 h) afford mixtures of $Ru(OC_6H_4CH{=}NR)H(CO)(PPh_3)_2$ (**I**) and $Ru(OC_6H_4CH{=}NR)_2(CO)(PPh_3)$. The latter products can be separated by fractional crystallisation and form orange–yellow crystals ($^{31}P\{^1H\}$ NMR, δ_{PPh_3} *ca.* 32–34 ppm(s)). In the absence of an X-ray crystal structure determination or any definitive spectroscopic evidence we are unable to establish the stereochemistry of these products. However, on the assumption that their formation from the hydrides (**I**) involves no stereochemical rearrangement of the coordination sphere, we tentatively assign stereochemistry (**II**). The same Schiff bases react with $RuHCl(CO)(PPh_3)_3$ in boiling 2-methoxyethanol to afford the bright yellow complexes $Ru(OC_6H_4CH{=}NR)Cl(CO)(PPh_3)_2$ together with significant amounts of the hydrido complexes $Ru(OC_6H_4CH{=}NR)H(CO)(PPh_3)_2$ (**I**, M = Ru), formed by base/alcohol (*i.e.* Schiff base/2-methoxyethanol) 'reduction' of the chloride ligands. These chloro complexes each display a ^{31}P NMR singlet at *ca.* 23 ppm and are therefore assigned *trans* phosphine stereochemistry (**IIIa** or **b**, M = Ru). Treatment of $Ru(CO)_3(PPh_3)_2$ with Schiff bases in boiling 2-methoxythanol also afford $Ru(OC_6H_4CH{=}NR)H(CO)(PPh_3)_2$ and, after more prolonged reactions, $Ru(OC_6H_4CH{=}NR)_2(CO)(PPh_3)$.

The Schiff bases also react with $RuCl_2(PPh_3)_3$ in warm benzene under aerobic conditions to give green paramagnetic ruthenium(III) products $RuCl_2(OC_6H_4CH{=}NR)(PPh_3)_2$; the same mixture when refluxed in the presence of triethylamine under anaerobic conditions, affords the known [2] complexes $Ru(OC_6H_4CH{=}NR)_2(PPh_3)_2$. These complexes are tentatively assigned structures (**IV**) (ν(RuCl) *ca.* 310 cm^{-1}), and (V) ($^{31}P\{^1H\}$ NMR *ca.* 31–32 ppm (s)) respectively, on the basis of the spectroscopic data and by analogy with related complexes [2, 6].



I



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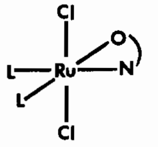
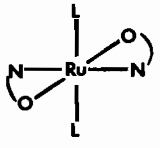
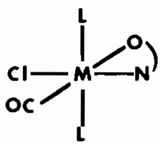


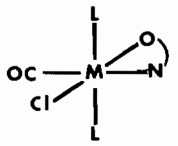
IIIa



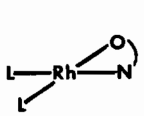
IIIb



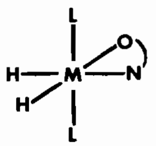
IV



V



VI



VII

L = PPh_3

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Analogous reactions with $OsH_2(CO)(PPh_3)_3$ and $OsHCl(CO)(PPh_3)_3$ afford the first mononuclear Schiff base complexes of osmium, $Os(OC_6H_4CH{=}NR)H(CO)(PPh_3)_2$ and $Os(OC_6H_4CH{=}NR)Cl(CO)(PPh_3)_2$ respectively. The hydrido complexes can be assigned stereochemistry (**I**, M = Os), on the basis of NMR data (^1H, δ_{OsH} *ca.* −10 ppm (t of d), $^2J(PH)$ *ca.* 19 Hz, $^4J(HH')$ *ca.* 2 Hz; $^{31}P\{^1H\}$, δ_{PPh_3} 17–20 ppm (s)). The chloro complexes appear to exist in two isomeric forms, a kinetically controlled *cis* phosphine isomer ($^{31}P\{^1H\}$ NMR AB pattern, δ_{PPh_3} *ca.* −4.5 and −5.5 ppm, $^2J(PP')$ *ca.* 32 Hz) and a thermodynamically favoured *trans* phosphine isomer (**IIIa** or **b**, M = Os) ($^{31}P\{^1H\}$ NMR δ_{PPh_3} *ca.* −3 ppm (s)).

Schiff bases react with $RhCl(PPh_3)_3$ in benzene at room temperature over a period of 24 h to yield yellow rhodium(I) products $Rh(OC_6H_4CH{=}NR)(PPh_3)_2$ which display NMR spectra ($^{31}P\{^1H\}$ AB pattern *ca.* 22.0 and 19.5 ppm, $^2J(PP')$ *ca.* 34 Hz, with additional doublet splittings $^1J(Rh{-}P)$ *ca.* 142 Hz) consistent with the expected square planar stereochemistry (**VI**). Treatment of $(RhCl(C_8H_{12}))_2$ with triphenylphosphine and Schiff base in benzene/methanol solution under dihydrogen affords the rhodium(III) complexes $Rh(OC_6H_4CH{=}NR)H_2(PPh_3)_2$, (R = Bz, Ph), as yellow microcrystals. NMR data, ($^1H\{^{31}P\}$, δ_{RhH} *ca.* −16 and −20 ppm (both d of d), $^1J(RhH)$ and $^2J(HH')$ *ca.* 12–18 Hz, $^{31}P\{^1H\}$, δ_{PPh_3} *ca.* 40–44 ppm (d), $^1J(RhP)$ *ca.* 120 Hz; $^{31}P\{aryl\ ^1H\}$, $^2J(PH)$ *ca.* 15 Hz are indicative of stereochemistry (**VII**, M = Rh). The corresponding iridium(III) complexes $Ir(OC_6H_4CH{=}NR)H_2(PPh_3)_2$ are obtained as yellow crystals by treatment of *mer*-$IrH_3(PPh_3)_3$ with Schiff bases in boiling toluene for *ca.* 4–5 h. NMR data, (^1H, δ_{IrH} *ca.* −26 ppm (t of d), $^2J(PH)$ *ca.* 16 Hz, $^2J(HH')$ *ca.* 7 Hz and *ca.* −20 ppm (t of d), $^2J(PH)$ *ca.* 18 Hz, $2J(HH')$ *ca.* 7 Hz and $^4J(HH'') \leq 2$ Hz; $^{31}P\{^1H\}$, δ_{PPh_3} *ca.* 18–21 ppm(s); $^{31}P\{aryl\ ^1H\}$, δ_{PPh_3} *ca.* 18–21 ppm (d of d), $^2J(PH)$ *ca.* 15 Hz) confirm stereochemistry (**VII**, M = Ir). Similar complexes have been obtained with a range of related ligands, including β-ketoamines and dibasic tetradentate Schiff bases. Good analytical data have been obtained for several representative examples of each type of complex reported.

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