Inorganica Chimica Acta, 45 (1980) L215–L216

Synthesis and Reactions of Some Diphenylphosphinous Acid Complexes of Ruthenium(II) and Platinum(II) Containing Dithioacid Ligands

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Received June 24, 1980

In recent years, a number of transition metal compounds containing the hydrogen-bonded $R_2POHOPR_2$ ligands (R = Ph, OMe, OEt) have been synthesised and some reactions of these complexes reported [1]. To date, however, the majority of these studies have been confined to complexes of palladium(II) and platinum(II). In this preliminary communication, we now wish to report the synthesis of some ruthenium(II) dimethyldithiophosphinate compounds which contain diphenylphosphinous acid ligands.* Some reactions of these complexes, together with those of the related $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ (R = Et, ^{i}Pr) [4] are also briefly described.

Several years ago, it was demonstrated that the complexes *cis*-$[Ru(S_2PR_2)_2(PPh_3)_2]$ (R = Me, Ph) underwent facile exchange reactions with phosphorus containing ligands (L′) of greater Lewis basicity to give *cis*-$[Ru(S_2PR_2)_2L'_2]$ (L′ = PMe_2Ph, $PMePh_2$) [5]. This exchange process has now been extended to synthesise a wider range of *cis*-$[Ru(S_2PMe_2)_2L'_2]$ (I) complexes (L′ = $PClPh_2$, PCl_2Ph, PCl_3, $P(OEt)Ph_2$, $P(OMe)Ph_2$) with the intention of then hydrolysing the *coordinated* P–Cl or P–OR bonds to produce complexes containing a range of $>$POHOP$<$ ligands (*cf.* related studies on Pt/R_2PCl compounds [6]). High yields of the neutral complexes (I) were obtained by refluxing in dry hexane, a suspension of $[Ru(S_2PMe_2)_2(PPh_3)_2]$ with an excess of L′. The products were characterised by elemental analyses, molecular weight and ir spectral measurements and ^1H and $^{31}P-\{^1H\}$ nmr studies confirmed the retention of a *cis*-configuration. However, unlike *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ which undergoes facile interconversion of optical isomers at ambient temperatures [5], all the products (except for L′ = $P(OEt)Ph_2$) exhibited stereochemical rigidity at this temperature although some scrambling was observed at elevated temperatures. Unfortunately all attempts to date to cleave these various P–X bonds *and* isolate clean products have met with little success, *e.g.* attempted acid hydrolysis of *cis*-$[Ru(S_2PMe_2)_2(P(OEt)Ph_2)_2]$ under very mild conditions gave paramagnetic ruthenium(III) compounds of unknown composition.

Therefore another approach was investigated, namely reaction of *cis*-$[Ru(S_2PMe_2)_2(PPh_3)_2]$ with a *large excess* of $PClPh_2$ in acetone to which *ca.* 10% water was added to convert the free chlorophosphine to $Ph_2P(O)H$. After refluxing for several hours, work-up gave a red, non-conducting crystalline solid formulated as $[Ru(S_2PMe_2)\{(Ph_2PO)_3H_2\}]$ (II) (yield *ca.* 30%) together with a large amount of white solid identified as $Ph_2P(O)C(OH)Me_2$. The latter arises from reaction of $Ph_2P(O)H$ with acetone and could be eliminated by carrying out the reaction in aqueous methanol. Evidence for compound (II) is based on elemental analyses and molecular weight determination [Found: C, 54.6; H, 4.6; M(in C_6H_6 by osmometry) 794. Required: C, 54.9; H, 4.6%; M 832]; ^{1}*H nmr in* $CDCl_3$ *at 298 K;* δ 2.00 ppm (d) $^2J_{PH}$ 12.0 Hz ($^-S_2PMe_2$); δ 6.50–8.00 ppm (m) ($\{Ph_2PO\}_3H_2$); δ 8.80 ppm (broad) ($\{Ph_2PO\}_3H_2$) and $^{31}P-\{^1H\}$ *nmr in* $CDCl_3$ *at 213–298 K,* δ 102.4 ppm (q) ($^-S_2PMe_2$); δ 122.8 ppm (d) ($\{Ph_2PO\}_3H_2$) $^3J_{PP}$ 4.4 Hz. Related five coordinate monomers $[Ru(S_2PR_2)(PMe_2Ph)_3]BPh_4$ (R = Me, Ph) have recently been synthesised, [R = Me; $^{31}P-\{^1H\}$ *nmr spectrum in* $CDCl_3$ *213–298 K*; δ 32.4 ppm (d) (PMe_2Ph); δ 110.3 ppm (q) ($^-S_2PMe_2$) $^3J_{PP}$ 3.6 Hz] and shown by X-ray analysis (for R = Ph) to have a distorted square pyramidal geometry [7]. Furthermore the existence of the interesting $R_2POHOP(R_2)OHOPR_2$ tridentate ligands have recently been verified by X-ray analysis on $[\{P(OMe)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{Ph_2PO)_3H_2\}]$ [2] and by characterisation of $[Co(\eta C_5H_5)(\{RO\}_2PO)_3H_2]BF_4$ (R= Me, Et) [8].

If $[Ru(S_2PMe_2)_2(PPh_3)_2]$ was reacted with only *small* amounts of $PClPh_2$ in aqueous methanol, an inseparable mixture of two products was obtained. Spectroscopic analysis showed that one of these was compound (II) and the other probably $[Ru(S_2PMe_2)(PPh_3)\{(Ph_2PO)_2H\}]$ (III) [$^{31}P-\{^1H\}$ *nmr in* $CDCl_3$ *at 298 K*; δ 52.4 ppm (td) $^2J_{PP}$ 37.1 Hz, $^3J_{PP}$ 4.4 Hz (PPh_3), δ 104.7 ppm (broad) ($^-S_2PMe_2$); 121.3 ppm (d.d) ($Ph_2POHOPPh_2$) $^2J_{PP}$ 37.1 Hz; $^3J_{PP}$ 2.9 Hz]. Reaction of this mixture with more $Ph_2P(O)H$ then gave (II) alone confirming that compound(III) is an intermediate in the formation of complex (II).

However, reaction of $[Ru(S_2PMe_2)_2(PPh_3)_2]$ with $Ph_2P(O)H$ *under the same conditions* gave a complex mixture of products (^{31}P nmr evidence) indicating that protonation and subsequent removal of a coordinated $^-S_2PMe_2$ group by the HCl released in the *in situ* hydrolysis of $PClPh_2$ is probably a key step in the

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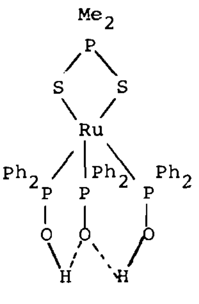
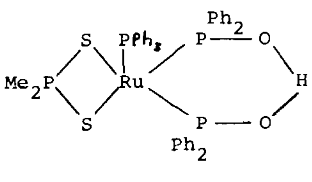
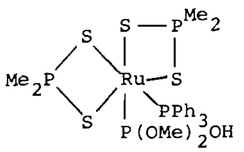
*The only other reported examples of ruthenium(II) complexes containing these types of ligand are $[\{P(OMe)Ph_2\}_2\{P(OH)Ph_2\}RuCl_3Ru\{(Ph_2PO)_3\}H_2]$ [2] and $[\{RuCl_2(NO)\{R(EtO)PO\}_2H\}]_2$ (R = OEt, Ph) [3].



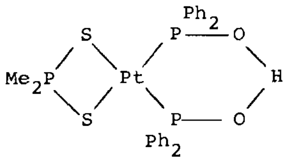
(II)



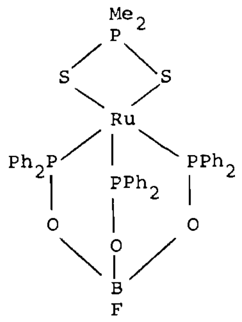
(III)



(IV)



(V)



(VI)

formation of compounds (II) and (III). In support of this observation, reaction of $[Ru(S_2PMe_2)_2(PPh_3)_2]$ with an excess of $P(OMe)_2(O)H$ in methanol gave a high yield of *cis*-$[Ru(S_2PMe_2)_2PPh_3(P\{OMe\}_2OH)]$ (IV) as the only product [Found: C 38.7; H 4.6; Required C, 39.8; H 4.7%; *$^{31}P-\{^1H\}$ nmr in $CDCl_3$ at 298 K*; δ 54.0 ppm (dt) $^2J_{pp}$ 48.2 Hz, $^3J_{pp}$ 5.5 Hz (PPh_3) δ 91.0 ppm (broad) (S_2PMe_2); δ 137.0 ppm (dt) $^2J_{pp}$ 48.2, $^3J_{pp}$ 7.3 Hz ($P\{OMe\}_2(O)H$)].

Some preliminary studies on reactions of compound (II) and the closely related $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ (V) (R = Et, ^iPr have also been made. Thus, reaction of (V) with $BF_3{\cdot}Et_2O$ gives $[Pt(S_2CNR_2)(Ph_2PO)_2BF_2]$ (*cf.* related compounds in ref. [1]) whereas with (II), reaction with $BF_3{\cdot}Et_2O$ appears to give $[Ru(S_2PMe_2)(Ph_2PO)_3BF]$ (VI) (*cf.* $[Co(\eta\text{-}C_5H_5)(\{RO\}_2PO)_3BF]BF_4$ [8]). Both compounds react with $VO(acac)_2$ to give $VO[(OPPh_2)_2Pt(S_2CNR_2)]_2$ and $VO[(OPPh_2)_2(HOPPh_2)Ru(S_2PMe_2)]_2$ respectively whereas with $Co(acac)_2$, preliminary evidence suggests that $Co[(OPPh_2)_2Pt(S_2CNR_2)]_2$ and $Co[(OPPh_2)_3Ru(S_2PMe_2)]_2$ are produced. Further reactions with a wider range of metal salts are now in progress.

Finally, the five coordinate complex (II) reacts with carbon monoxide under very mild conditions to give the six coordinate $[Ru(S_2PMe_2)CO\{(Ph_2PO)_3H_2\}]$ but longer reaction times also give some $[Ru(S_2PMe_2)(CO)_2\{(Ph_2PO)_2H\}]$.

Acknowledgement

We thank Johnson Matthey Ltd for loans of $RuCl_3xH_2O$ and K_2PtCl_4, the University of Edinburgh for financial assistance (IWR), Messrs D. Anderson and N. J. Duck for experimental assistance, Professor D. M. Roundhill of Washington State University, USA for helpful discussions and provision of laboratory facilities and NATO for a travel grant (TAS).

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