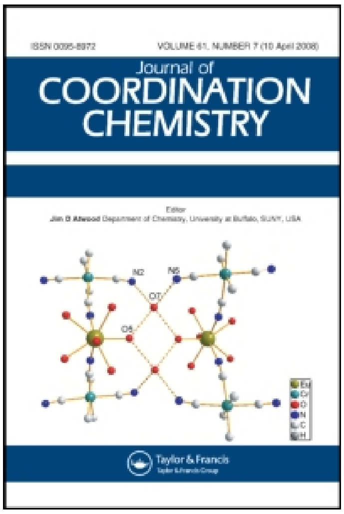

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RUTHENIUM(II) COMPLEXES WITH POLYDENTATE PHOSPHINES

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RUTHENIUM(II) COMPLEXES WITH POLYDENTATE PHOSPHINES

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Ruthenium(II) complexes of $C_6H_5P[CH_2 \cdot CH_2 \cdot P(C_6H_5)_2]_2$ triphos, $(C_6H_5)_2 \cdot P \cdot CH_2 \cdot CH_2 \cdot P(C_6H_5) \cdot CH_2 \cdot CH_2 \cdot P(C_6H_5) \cdot CH_2 \cdot CH_2 \cdot P(C_6H_5)_2$ tetraphos-1 and $P[CH_2 \cdot CH_2 \cdot P(C_6H_5)_2]_3$ tetraphos-2 are reported. The treatment of $RuCl_2(PPh_3)_3$ with triphos, tetraphos-2(tet-2), and tetraphos-1(tet-1), in benzene solution resulted in the formation of the complexes $RuCl_2$(triphos), $RuCl_2(PPh_3)$tet-2 and [RuCl(tet-1)]Cl respectively. Ruthenium(III) chloride hydrate in dimethylformamide reacts with triphos, tet-1 and tet-2 to yield the complexes $RuCl_2$(CO)triphos, $[RuCl_2(CO)_2]_2L$ (L = tet-1 or tet-2), respectively. The reaction of $RuCl_2(DMSO)_4$ with these ligands in benzene and methanol solution respectively gave the complexes $RuCl_2(DMSO)_2$ (triphos), [RuCl(DMSO)L]Cl (L = tet-1 or tet-2). The complexes thus obtained undergo reaction with carbon monoxide and hydrogen to yield the corresponding carbonyl and hydrido complexes. The complexes failed to react with molecular oxygen.

INTRODUCTION

During the last fifteen years tertiary phosphines have attained importance in coordination chemistry[1], because many of their metal complexes have been shown to possess unusual chemical properties of importance in such diverse areas as homogeneous hydrogenation[2], oxygen transfer[3], and nitrogen fixation[4]. The ligands $C_6H_5P[CH_2 \cdot CH_2 \cdot P(C_6H_5)_2]_2$ triphos, $(C_6H_5)_2P \cdot CH_2 \cdot CH_2 \cdot P(C_6H_5). CH_2 \cdot CH_2 \cdot P(C_6H_5) \cdot CH_2 \cdot CH_2 \cdot P(C_6H_5)_2$ tetraphos-1 and $P[CH_2 \cdot CH_2 \cdot P(C_6H_5)_2]_3$ tetraphos-2 were first prepared by King and Kapoor[5] and their metal complexes with several metal ions have been reported. The isomeric ligands tet-1 and tet-2 contain, respectively the linear P–P–P–P and tripod $P–P_3$ arrangements of the donor phosphorous atoms. Iridium(I) and rhodium(I) complexes of the tripod ligand 1,1,1,tris-(diphenylphosphinomethyl)ethane TDPME have been reported by Siegel et al[6]. Venanzi and coworkers[7] studied several complexes of TDPME and closely related ligands. Complexes of the tripod tetradentate ligands $[(CH_3)_2As \cdot CH_2 \cdot CH_2 \cdot CH_2]_3As$ were reported by Barclay and Barnard[8] and by Benner and Meek[9]. Benner *et al*[10] investigated the complexes of $[CH_3As \cdot CH_2CH_2]_3P$. Khan and Martell[11] have reported recently the iridium(I) and rhodium(I) complexes of triphos, tet-1 and tet-2. Since polytertiary phosphines improve stereochemistries and reactivity patterns on the metal ion that are not otherwise possible with monodentate phosphines, a study of the octahedral d^6 complexes of ruthenium(II) were considered important for the present studies. In the present paper we report the synthesis of some new complexes formed by the treatment of $RuCl_2(PPh_3)_3$, $RuCl_3 3H_2O$ and $RuCl_2(DMSO)_4$ with triphos, tet-1 and tet-2 and reactions of the resulting complexes with carbonmonoxide, hydrogen and oxygen.

EXPERIMENTAL

The ligands triphos, tetraphos-1 and tetraphos-2 were purchased from Pressure Chemical Corporation Inc., ruthenium chloride was obtained from Alfa Inorganics. The complexes $RuCl_2(PPh_3)_3$[12] and $RuCl_2(DMSO)_4$[13] were synthesized by standard procedures. Carbonmonoxide and hydrogen gas were prepared and purified by standard procedure. Oxygen was obtained commercially and purified. Microanalysis of the complexes was performed by Australian Microanalytical Service CSIRO Canberra, Australia. The infrared spectra were recorded on a Beckman IR-12 spectrophotometer using Nujol Mulls on polyethylene plates. The nmr spectra of the solution of the samples in deuterated chloroform and in deuterated dimethyl sulfoxide were recorded with a a Varian A-60 spectrometer. Conductance data were obtained in dimethyl acetamide (DMA) solution using

TABLE I
Analytical data for the Ru(II) complexes of polydentate phosphines

			Analysis %								
			C		H		Cl				
Entry	Compound	Color	C	F	C	F	C	F	yield	M.P(°C)	Molar conductance (ohm^{-1}, cm^2, equiv^{-1})
1	$RuCl_2$(triphos)	Light green	57.70	58.79	4.67	4.74	10.06	9.52	85	220–226	20
2	$RuCl_2(PPh_3)$(tet-2)	Yellow	65.22	65.40	5.16	5.26	6.43	6.43	86	95–100	30.81
3	[RuCl(tet-1)]Cl	Yellowish green	59.85	60.38	4.98	4.86	8.43	8.18	88	235–240	50.06
4	$RuCl_2$(CO)(triphos)	Brown	57.20	58.10	4.80	5.00	9.60	8.90	85	195–200 (decomposed)	23
5	$[RuCl_2(CO)_2]_2$(tet-1)	Buff	49.34	51.09	4.00	5.07	13.20	12.89	86	270–275 (decomposed)	9.7
6	$[RuCl_2(CO)_2]_2$(tet-2)	Yellowish brown	49.34	50.10	4.00	4.20	13.20	12.90	84	118–122	19.08
7	$RuCl_2(DMSO)_2$(triphos)	Yellowish brown	52.10	51.00	5.22	4.95	8.53	10.10	87	208–210 (decomposed)	16.03
8	[RuCl(DMSO)(tet-1)]Cl	Yellow	57.38	56.77	5.21	4.81	7.71	8.30	86	228–232 (decomposed)	63.5
9	[RuCl(DMSO)(tet-2)]Cl	Light yellow	57.38	56.03	5.21	5.09	7.71	8.50	87	224–228	47.5

C = calculated; F = found.

a Systronics conductance bridge and a cell which had been calibrated with 0.1 M aqueous potassium chloride solution. All the preparations were carried out under an oxygen free nitrogen atmosphere using Schlenk tube techniques.

Synthesis of Complexes

The synthesis of complexes *1–3* of Table I involved the addition of a 0.01 M solution of $RuCl_2(PPh_3)_3$ in dry benzene to a 0.01 M solution of triphos, tet-1 and tet-2 respectively. The resulting solution was then refluxed for about six hours. The solutions were concentrated to a small volume under vacuum, a small amount of acetone added and the products precipitated with petroleum ether. The complexes, $RuCl_2$(triphos) $RuCl_2(PPh_3)$(tet-2) and [RuCl(tet-1)]Cl thus obtained were washed with ether and dried.

Complexes *4–6* were synthesized by a general procedure which involved the addition of 0.01 mol of ruthenium chloride hydrate to about 50 ml of dimethyl formamide (DMF). To this was added 0.01 mol of triphos, 0.01 mol of tet-1 and 0.01 mol of tet-2 respectively and the resulting solution refluxed for about six hours. The solution turned light brown in the case of triphos and yellowish brown in the case of tet-1 and tet-2. The solutions were cooled to room temperature and the excess of DMF removed with the help of a rotary vacuum evaporator at 1 mm and 80°C. Addition of anhydrous methanol precipitated the complexes $RuCl_2$(CO) (triphos), $[RuCl_2(CO)_2]_2$(tet-1) and $[RuCl_2(CO)_2]_2$ (tet-2) as brown, buff and yellowish brown products, respectively. The complexes were collected by filtration, washed with ether, and dried.

Complexes *7–9* were prepared by adding 0.005 mol of $RuCl_2(DMSO)_4$ in 50 ml benzene methanol (1;1) to 0.01 mol of triphos, tet-1, and tet-2, respectively and refluxing the solution for about six hours. The initial color changed from orange to yellow in the case of triphos and from dark yellow to light yellow in case of tet-1 and tet-2. The solutions were evaporated to a small volume under vacuum, dissolved in acetone and the products precipitated with ether. The products $RuCl_2(DMSO)_2$ (triphos), [RuCl(DMSO)L] Cl (L = tet-1 or tet-2) were collected by filtration, washed with ether and dried.

Carbonylation of Complexes

About 0.010 mol of the complexes *1–4*, *7–9* were dissolved in dry chloroform and a stream of carbon monoxide was passed through the solution till there was no further color change. Addition of petroleum ether precipitated the products which were filtered and dried. Complex *1* on carbonylation gave [RuCl(CO)(triphos)] Cl. Carbonylation of *2* and *8* did not yield any carbonylated products. Complexes *3*, *7* and *9* however afforded the products *11*, *12* and *13*, respectively.

Hydrogenation of Complexes

Molecular hydrogen was bubbled through a 0.010 M chloroform solution of the complexes *1–3*, *7–9* for about thirty hours. Complexes *2* and *9* did not react with molecular hydrogen. Complexes *1*, *3*, *7* and *8* however yielded the monohydrides *14*, *15*, *16* and *17* respectively.

TABLE II
Analytical data for reaction products with carbonmonoxide and molecular hydrogen of Ru(II) complexes of polydentate phosphines

			Analysis %					
			C		H		Cl	
Entry	Compound	Color	C	F	C	F	C	F
10	[RuCl(CO)(triphos)] Cl	Greenish yellow	57.20	57.90	4.80	4.95	9.60	8.85
11	[RuCl(CO)(tet-1)] Cl	Light yellow	59.30	60.00	4.82	4.73	8.16	7.65
12	$RuCl_2$(DMSO)(CO)(triphos)	Yellow	51.23	50.87	4.71	4.90	8.74	7.90
13	$[Ru_2Cl_2(DMSO)_2(CO)_3$(tet-2)]Cl_2	Light yellow	46.88	46.75	4.30	4.24	11.32	10.85
14	Ru(H)Cl(triphos)	Green	60.81	59.78	5.06	5.20	5.21	4.96
15	Ru(H)Cl(tet-1)	Yellow	62.44	61.89	5.32	5.40	4.33	3.76
16	Ru(H)Cl$(DMSO)_2$(triphos)	Yellow	53.32	52.97	5.56	5.70	4.23	3.67
17	Ru(H)Cl(DMSO)(tet-1)	Yellow	59.67	58.88	5.53	5.45	3.95	3.58

C = calculated, F = found.

TABLE III
Infrared spectra of polytertiary phosphine complexes of ruthenium(II) and the reaction products with carbonmonoxide and molecular hydrogen

Entry	Compound	ν(M–Cl)cm^{-1}	ν(M–DMSO)cm^{-1}	ν(CO)cm^{-1}	ν(M–H)cm^{-1}	Other bands
1	$RuCl_2$(triphos)	332(m)				500(m), 528(s), 545(s), 620(m)
2	$RuCl_2(PPh_3)$(tet-2)	250(m), 270(m)				515(v.s), 610(m), 670(m), 690(s)
3	[RuCl(tet-1)]Cl	270(mbr)				528(v.s), 620(m), 670(m)
4	$RuCl_2$(CO)(triphos)	265(m), 280(m)		1960(m)		500(m), 525(v.s), 550(s), 2030(ω)
5	$[RuCl_2(CO)_2]_2$(tet-1)	298(m)		1960(m), 2060(w)		482(s), 520(v.s), 535(s), 585(s), 650(s)
6	$[RuCl_2(CO)_2]_2$(tet-2)	325(m)		1990(s), 2035(s)		500(s), 535(s), 580(m)
7	$RuCl_2(DMSO)_2$(triphos)	265(m), 275(m)	490(m), 1025(m), 1095(s), 1430(v.s)			430(m), 530(s), 690(s).
8	[RuCl(DMSO)tet-1]Cl	250(br)	500(s), 1025(m), 1095(s), 1430(s)			516(s), 675(m), 690(s)
9	[RuCl(DMSO)(tet-2)]Cl	270(br)	480(s), 1020(m), 1090(s), 1430(s)			416–436(br), 520(v.s), 670(m)
10	[RuCl(CO)(triphos)]Cl	270(m)		1960(m)		500(s), 525(m), 560(m), 670(m), 700(s), 2025(ω)
11	[RuCl(CO)tet-1]Cl	260(m)		1940(m)		525(m), 620(m), 670(m)
12	$RuCl_2$(DMSO)(CO)(triphos)	260(m), 270(m)	485(m), 1025(m), 1095(m), 1430(s)	1950(s)		425(m), 520(s), 690(s), 2035(ω)
13	$[Ru_2Cl_2(DMSO)_2(CO)_3$(tet-2)$]Cl_2$		480(s), 1025(m), 1095(s), 1430(s)	1870(m), 1930(m)		530(m), 670(m), 2020(ω)
14	Ru(H)Cl(triphos)	265(m)			1930(m)	525(m), 545(s), 620(m), 690(s)
15	Ru(H)Cl(tet-1)	260(m)			1920(m)	525(s), 690(m)
16	Ru(H)(Cl)$(DMSO)_2$(triphos)	245(m)	490(s), 1020(m), 1100(s), 1450(s)		1945(m)	430(m), 690(s)
17	Ru(H)Cl(DMSO)(tet-1)	250(m)	480(m), 1020(m), 1100(s), 1450(s)		1950(m)	515(s), 690(s), 740

key: v.s = very strong; s = strong; m = medium; w = weak; br = broad; sh = shoulder.

TABLE IV
Proton nmr spectra* of Ru(II) complexes of polytertiary phosphines

		Phenyl protons	Methylene protons	Methyl protons/ methylene protons
1	$RuCl_2$(triphos)	3.35(m), 3.50(s)	9.00(m)	
2	$RuCl_2(PPh_3)$(tet-2)	3.50(t)	8.25(s), 8.80(m)	
3	[RuCl(tet-1)]Cl	3.50(m)	8.30(s)	
4	[RuCl(DMSO)(tet-1)]Cl	2.90(m)		6.80(s), 7.40(d), 7.50(q), 7.80(s)
5	[RuCl(DMSO)(tet-2)]Cl	2.60(m), 3.00(m)		6.40(s), 7.25(d), 7.80(s)

key: d = doublet; s = singlet; t = triplet; m = multiplet; q = quartet;* τ values.

Oxygenation of Complexes

Molecular oxygen was passed through a 0.01 M chloroform solution of the complexes *1, 7–9* for about forty eight hours. The infrared spectra recorded after passing oxygen were identical with parent complexes, indicating that oxygen has failed to react with these complexes.

RESULTS

Table III presents the infrared spectra of the nine complexes and their reaction products with carbonmonoxide and hydrogen. Assignment of the carbonyl (C–O) stretch and metal-hydride frequencies were based on comparison with known spectra of related compounds[5(a,b)]. The proton magnetic resonance spectra of *1, 3, 8* and *9* are presented in Table IV. Insolubility of the other complexes in common organic solvents prevented the measurement of their nmr spectra.

Carbonylation of Complexes

The complex $RuCl_2$(triphos) on carbonylation forms [RuCl(CO)(triphos)] Cl. The monocarbonyls $RuCl_2$(DMSO)(CO)(triphos) and [RuCl(CO)(tet-1)] Cl were confirmed by the appearance of peaks around 1950 cm^{-1} and 1940 cm^{-1}, respectively. The complex [RuCl(DMSO)(tet-2)] Cl yielded a carbonyl of the type $[Ru_2Cl_2(DMSO)_2(CO)_3$(tet-2)$]Cl_2$ containing both bridged and nonbridged carbonyls. In the case of $RuCl_2(PPh_3)$(tet-2) and [RuCl(DMSO)(tet-1)] Cl complexes the infrared spectra after carbonylation were identical with the spectra of the parent complex in the 1920–2100 cm^{-1} range, indicating that no carbonylation had taken place.

Hydrogenation of Complexes

Hydrogenation of the complexes *1, 3, 7* and *8* in chloroform resulted in the formation of the monohydrides (entries 14 to 17). The hydrides were found to be quite stable. In case of $RuCl_2(PPh_3)$(tet-2) and [RuCl(DMSO)(tet-2)] Cl however there is no hydride formation.

DISCUSSION

The displacement of the coordinated unidentate phosphine ligands from $RuCl_2(PPh_3)_3$ by the polytertiary phosphines triphos, tet-1 and tet-2 afforded the most convenient method for the synthesis of polytertiary phosphine complexes of ruthenium(II). Conductivity measurements indicate that complexes *3, 8* and *9* are 1:1 electrolyte (conductance in DMA >40 ohm^{-1}, cm^2, $equiv^{-1}$) and complex *5* is a non-electrolyte. The other complexes show appreciable conductivities (15–23 ohm^{-1}, cm^2, $equiv^{-1}$), probably due to solvolysis by dimethyl acetamide. In an attempted preparation of a ruthenium(II) complex of triphos by the interaction of ruthenium(III) chloride and triphos, King *et al*[5(a,b)] had obtained a chloro-bridged dimer of the composition $[RuCl_2(triphos)_2]_2$. In the present work, displacement of triphenylphosphine from $RuCl_2(PPh_3)_3$ by triphos however yielded the monomeric complex *1* in a very good yield (about 85%). Although a precise structure can not be assigned for the complex *1*, it may possess an approximate square pyramidal structure with phosphorous atoms in cis-cis-*trans* configuration and *trans* halogens. A single infrared M–Cl peak is expected for this configuration as is observed in the complex. In the proposed structure the two trans phosphorus atoms are equivalent but different from the third phosphorus atom. This is supported by the nmr spectrum of the complex in which there is a multiplet centered at 3.35 τ due to the phenyl protons of the two equivalent phosphorus atoms and a singlet at 3.50 τ due to the phenyl protons of third phosphorus. The peak at 9.00 τ can be attributed to the methylene protons of the ligand.

Monocarbonyl *10* is formed from complex *1* by the displacement of one of the coordinated chloride. The conductivity of the complex (55 ohm^{-1}, cm^2, equiv^{-1}) in DMA suggests[16] the complex to have the formula [RuCl(CO)(triphos)] Cl. The reaction with molecular hydrogen proceeds similarly, yielding a monohydrido complex *14*. Complex *1* is novel in that it is very stable towards molecular oxygen and in this respect it behaves in a manner completely different from $RuCl_2(PPh_3)_3$ which reacts with molecular oxygen to give a number of products[15]. The complex is thus a good candidate for a hydrogenation catalyst.

In the infrared spectrum of complex *2*, two peaks corresponding to M–Cl stretch appeared at 250 and 270 cm^{-1}, indicating that the halogens have a cis configuration. The lower M–Cl frequencies of the complex are expected because they are trans to phosphorus[17]. Tetraphos-2 must be coordinated as a terdentate ligand, the remaining coordination position on the metal ion being occupied by the triphenylphosphine and the two cis chloride groups as shown in Fig. 1. In complex *2*, tetraphos-2 may have a meridonal disposition of phosphorus atoms with one unbound phosphorus atom. This complex contains three types of coordinated phosphorus atoms; phosphorus atoms with two C_6H_5 groups, the unbound phosphorus atom of tet-2 and the phosphorus atom of triphenylphosphine. The triplet at 3.50 τ could be due to the overlap of peaks expected from the phenyl protons of these phosphorus atoms. The multiplet at 8.80 τ may be due to the methylene protons of the coordinated phosphorus atoms and the singlet at 8.25 due to the methylene protons of uncoordinated phosphorus.

Complex *3* is a 1:1 electrolyte in DMA (Table I) and could be formulated as [RuCl(tet-1)] Cl. Since tet-1 is a linear molecule it may be possible for this ligand to coordinate four positions in a trigonal bipyramid leaving one axial position vacant for chlorine or alternately, the four phosphorus atoms may occupy *cis-cis-cis-trans* position on a square pyramid. In both the cases chlorine is trans to phosphorus which explains the observed Ru–Cl frequency. The nmr spectrum, however, cannot distinguish the two possibilities. The second possibility appears to be more feasible, since this will explain the addition of carbonyl group on the vacant coordination position in the complex. This is further supported by the fact that the monocarbonyl *11* (Table III) is also a 1:1 electrolyte in DMA (57 ohm^{-1}, cm^2, equiv^{-1}). Reaction of complex *3* with molecular hydrogen gives a monohydrido complex *15* which may have the same structure as the carbonyl *11*.

Complex *4* is similar in composition to complex *10* but differs in the fact that it is a non-electrolyte in DMA. The structure of the complex may be represented as in Fig. 2. In the IR spectrum of the complex the chlorine trans to the carbonyl group appears at 280 cm^{-1} and chlorine trans to phosphorus at 265 cm^{-1}.[17]

In both the binuclear complexes *5* and *6*, the carbonyl groups appear to be cis and the halogens are trans. The difference in νRu–Cl of the two complexes may be attributed to the difference in nature of bridging and stereochemical requirements of tet-1

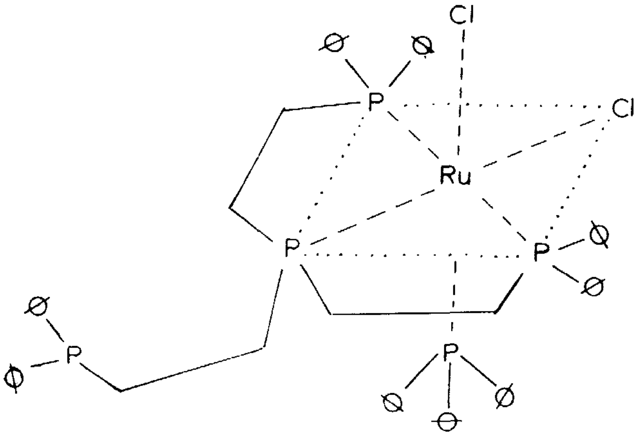


FIGURE 1 $RuCl_2(PPh_3)(tetraphos\text{-}2)$

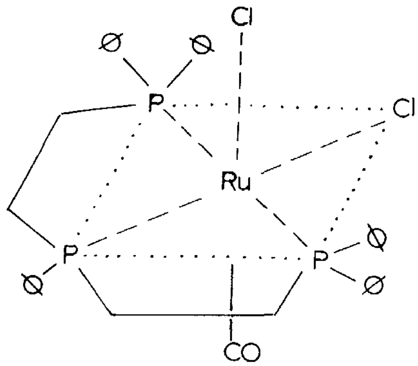


FIGURE 2 $RuCl_2(CO)(triphos)$

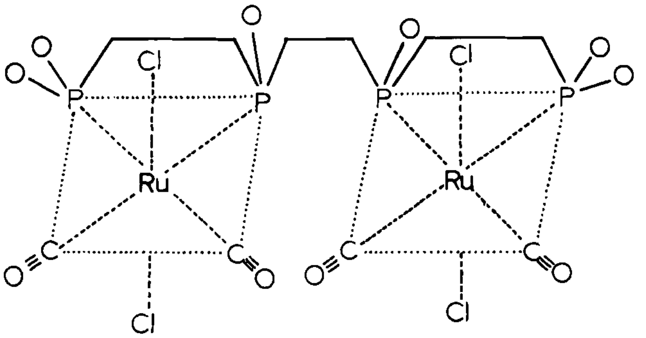


FIGURE 3 $[RuCl_2(CO)_2]_2$(tetraphos-1)

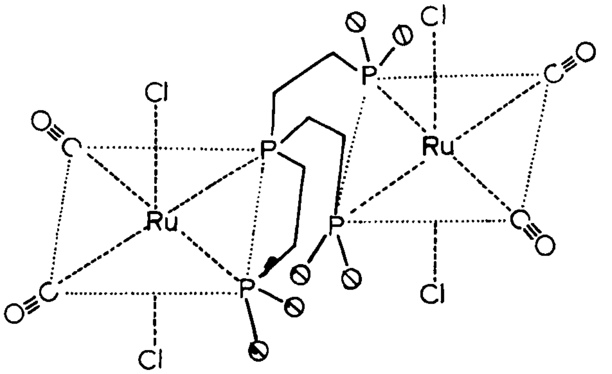


FIGURE 4 $[RuCl_2(CO)_2]_2$(tetraphos-2)

and tet-2 which may cause some environmental effect in Cl–Ru–Cl group in the two complexes. The bridging of the $RuCl_2(CO)_2$ moiety by tet-1 and tet-2 ligands in the binuclear species *5* and *6* is shown in Fig. 3 and 4, respectively.

The complex $RuCl_2(DMSO)_4$ reacts with triphos, tet-1 and tet-2, respectively, to yield complexes 7–9. The IR spectra of these complexes show strong band around 1090 cm^{-1}, indicative of S-bonded DMSO[18], but no band around 900 cm^{-1} which could be attributed to 0-bonded DMSO[19].

In complex *7* the coordinated halogens have cis configuration as evident by the IR spectrum. On carbonylation one of the coordinated DMSO is displaced by the carbonyl group to give complex *12*. The hydrogenation of *7* proceeds through the displacement of one of the coordinated chlorines to yield a monohydride *16*.

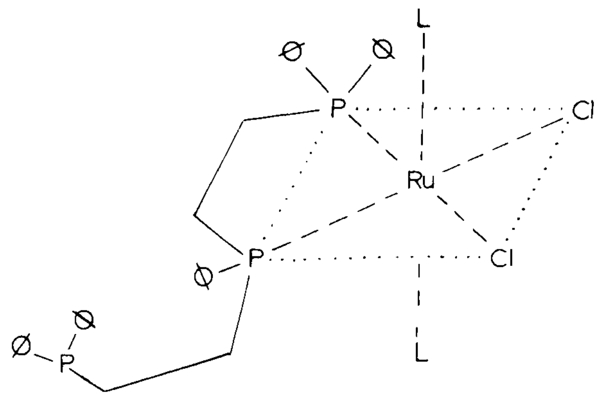
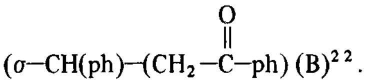


FIGURE 5 $RuCl_2(DMSO)_2$(triphos)

Complex *8* may have an octahedral structure with all the phosphorus atoms of the ligand tet-1 in one plane and a chlorine trans to DMSO group as shown by its IR spectrum. The X-ray structure of some of the octahedral Ir(III) complexes[20] $(t_2g)^6$ systems have indicated that DMSO is quite high in trans effect and it is even more than a tertiary phosphine. This result is arrived at by comparing the bond distances of trans chlorine-ligand in the complexes; mer-$IrCl_3(Pme_2ph)_3$(A)[21], and $IrCl_2(DMSO)_2$-



$(\sigma\text{–}CH(ph)\text{–}(CH_2\text{–}\overset{\overset{O}{\|}}{C}\text{–}ph)$ (B)[22]. In case of complex A where Cl is trans to phosphine Ir–Cl bond length is 2.36A, whereas it is 2.38A in complex B in which Cl is trans to S-bonded DMSO. The high trans effect of S-bonded DMSO is further supported by the recent X-ray studies on complexes $RuCl_2(DMSO)_4$[23] (C), and $[RuCl_3(DMSO)_3]$ $[(NH_2me_2)]$[19] (D). The Ru–Cl bond lengths in these two complexes, where Cl is trans to S-bonded DMSO are 2.435A in C and 2.426A (mean value) in D. These are significantly longer than the complexes where chlorines are mutually trans, e.g., 2.390A in $RuCl_3(N_2\text{–}C_6H_4Me)(Pph_3)_2(Me_2O)$. Hence the lower frequency of Ru–Cl in *8* as compared to *9* can be accounted in terms of a higher trans effect of a S-bonded DMSO than phosphine. The phenyl protons of the tet-1 are equivalent and appear as a multiplet centered at 2.90τ,

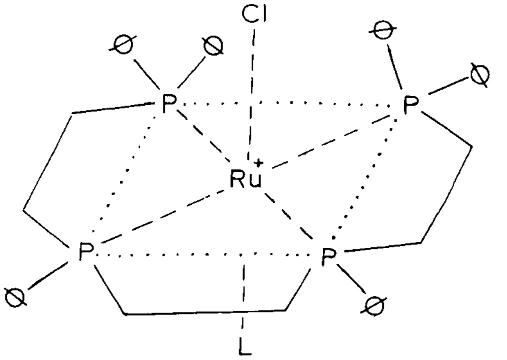


FIGURE 6 $[RuCl(DMSO)(tetraphos\text{-}1)]^+$

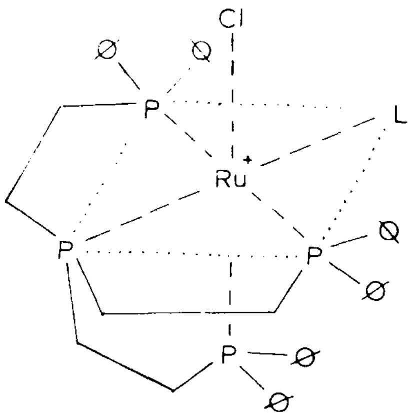


FIGURE 7 [RuCl(DMSO)(tetraphos-2)]$^+$

and methylene protons at 7.40τ. The methyl protons of S-bonded DMSO appear at 6.80τ. On hydrogenation complex *8* yields a hydrido complex *17*.

In complex *9* there are two sets of $-PQ_2$ groups which appear in the nmr spectrum as multiplets centered at 2.60τ and 3.00τ, the methylene protons of tet-2 appear at 7.25τ. The peaks due to the methyl protons of S-bonded DMSO appear at 6.40τ. Complex *9* on carbonylation yielded a carbonyl of composition $[Ru_2Cl_2(CO)_3(DMSO)_2(tet\text{-}2)]Cl_2$, which appears to contain both bridging and nonbridging carbonyl groups. The bridging carbonyls appear at lower frequency than nonbridging (Table III).

Ruthenium(II) complexes of polytertiary phosphine react with molecular hydrogen and as such are possible catalysts in homogeneous hydrogenation reactions. Investigation of catalytic properties of metal complexes described in this paper are in progress.

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